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MANUAL OF CHEMISTRY.

BY ARTHUR P. LUFF, M.D., B.Sc.,
F.R.C.P.

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A MANUAL

OF

CHEMISTRY

INORGANIC AND ORGANIC

WITH AN APPENDIX COVERING THE SYNOPSES OF THE CONJOINT BOARD AND THE SOCIETY OF APOTHECARIES

BY

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ILLUSTRATED WITH 40 ENGRAVINGS

CASSELL AND COMPANY, LIMITED
LONDON, PARIS, NEW YORK & MELBOURNE. MCMIV

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19246325

First Edition May 1892. *Reprinted* 1895, 1897.
Revised Edition 1900. *Reprinted* 1901, 1904.

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PREFACE.

This book is intended as a guide to the study of chemical science for the use of students of medicine. Now that Chemistry, and especially Organic Chemistry, has become so vast a science, the student of medicine is, on the one hand, apt to find himself out of his depth in attempting the perusal of the larger handbooks on the subject; and, on the other hand, with many of the smaller works, excellent in their way, he is hampered by omission of matter essential to the successful after-study and practice of medicine. This book has therefore been written to bring together in a concise form those portions of chemical science that directly or indirectly bear on the study and practice of medicine.

To gauge correctly the wants of the student of medicine, and to appreciate rightly the position that must be assigned to the study of Chemistry amongst his multifarious work, can, in my opinion, be best done by one who has himself been through the courses of study and work required for qualifying in medicine. I have therefore undertaken the task of writing this book in the hope that it may supply a long-felt want, and that it may assist the student in acquiring a sound knowledge of the fundamental principles of Chemistry.

A. P. L.

31, *Weymouth Street, W.*

PREFACE TO REVISED EDITION.

HAVING used this Manual as a text-book in my Conjoint classes at the London Hospital for some years, it was with much pleasure that I undertook the task of revising the work, and incorporating in it such new facts and methods as the ever-increasing progress of the science had rendered necessary.

I have adhered, as far as possible, to the original arrangement of the book. The metals, however, are discussed in the groups into which they fall in the Newlands and Mendeljeeff classification. Much of the organic part has been re-written, and short accounts of the vapour-density apparatus of Victor Meyer and of Beckmann's method of determining the depression of the freezing point and their use in fixing molecular weights, have been inserted. I have given brief notes on some of the results of Fischer's work on the sugars and on the composition of some of the complex synthetic substances now used in medicine.

In the practical part will be found the tables which have been in use in this laboratory for some time, together with some notes on the typical salts, whose preparation is required at the Conjoint examination.

Temperatures throughout the work are given in the centigrade scale.

F. J. M. P.

Chemical Laboratory,
London Hospital Medical College,
Turner Street, E. Jan., 1900.

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and can be acted on by a force.

MANUAL OF CHEMISTRY.

Part I.

INTRODUCTION TO THE STUDY OF CHEMISTRY.

CHAPTER I.

Matter—Solids—Liquids—Gases—Latent Heat—Mixtures and Chemical Compounds—Chemical Attraction—Heat produced by Chemical Action.

Matter.—In order to commence the study of Chemistry clearly and definitely, it is absolutely neces-
sary that the student should understand what matter 1.
is, the different forms in which it exists, and the laws 2.
which cause the existence of these different forms of 3.
matter.

The three forms of matter.—Matter is that which is evident to the senses, and it exists in three forms: viz. the *solid*, *liquid*, and *gaseous*. Any one of these forms of matter can be converted into either of the other two; thus, by melting *solid* ice it becomes *liquid* water, and by boiling the liquid water *gaseous* steam is produced. The particles of all bodies are
under the influence of two forces: one a **force of** 1.
attraction (otherwise known as **cohesion**) and the
other a **force of repulsion** (which, as will be pre- 2
sently explained, is closely connected with **latent**

heat); and according to the distribution of these forces of attraction and repulsion the different forms of matter result. If one of the forces is in excess of the other, one of the two extreme forms of matter (the solid or the gaseous) results; if the two forces are equally balanced, then the intermediate form of matter (the liquid) is the result.

Thus in all **solids** the force of attraction of the particles for one another is greater than the force of repulsion. The peculiarity of the solid form of matter is that the relative positions of its particles cannot be changed without the expenditure of more or less force; solids therefore tend to retain whatever form they may happen to possess.

In **liquids** the forces of attraction and repulsion of the particles are equally balanced. The distinctive peculiarity of the liquid state is that the particles readily glide over one another, and assume the shape of the vessel containing the liquid.

In **gases** the force of repulsion exercised by the particles is considerably greater than the force of attraction. The distinctive character of the gaseous state is that the particles are continually undergoing a struggle to occupy a larger space. It will now be easy for the student to understand why a gas can be compressed by additional pressure and expanded by partial removal of pressure: the compression of a gas being brought about by the mechanical force employed overcoming the repulsive force of its particles; and the expansion of a gas being caused by the repulsive force of the particles for one another coming into play, when the pressure is removed.

It must not be supposed that the particles of any one of these forms of matter are in absolute contact with one another, although such is a common opinion with regard to solids and liquids. That solids are in reality porous, that the particles are not absolutely

1. close together, is proved by hammering or powerfully pressing them, when they will be found to occupy a smaller bulk than they did previous to being submitted to pressure; and again is proved by what is
2 technically called the "sweating" of iron in the Bramah hydraulic press, where water under powerful pressure actually is forced through the pores of a stout iron cylinder, although to the eye the iron appears perfectly compact and homogeneous. That liquids have spaces between their particles is best ?
? proved by mixing certain liquids together, when a contraction in bulk takes place. If alcohol and water be mixed together, a diminution in volume occurs, the particles getting closer together than they formerly were, due to a molecular combination of the alcohol with the water; thus, in making proof spirit, 100 fluid ounces of rectified spirit are mixed with 10
60 fluid ounces of water, yet only 156 fluid ounces 6
of proof spirit result, a contraction of about 2½ per 16
cent. having taken place.

The student having now become acquainted with the different forms of matter, the next thing for him to understand is how and under what conditions any one form of matter is capable of being converted into another. Heat is the agent necessary for the transformation of one form of matter into another, and it is the addition or abstraction of heat that brings about the change of state in any form of matter. If a piece of roll sulphur (representing the solid form of matter) be heated in a test-tube or flask, it will first melt to a yellow fluid (representing the liquid form of matter), and this on further heating will boil away, forming a heavy vapour of a reddish-brown colour (representing the gaseous form of matter); heat is therefore the agent that has converted the solid into a liquid, and the liquid into a gas or vapour. Now, if part of the heat be abstracted from the sulphur vapour, this will condense to a syrupy fluid; and this fluid on further cooling (that is, on further abstraction of heat) will solidify to a mass of solid sulphur. From these simple experiments the following general law can be deduced:—

Either the addition or abstraction of heat is necessary for the conversion of any one form of matter into another form.

Latent heat.—The heat which is stored up in liquids and gases, and which prevents their change of state, is called *latent heat*. Latent or hidden heat is that heat which cannot be detected by the thermometer, which is doing other work than that of making itself sensible to the thermometer: viz. preventing the change of state of the body in which it is stored up. Thus, on applying heat to the piece of roll sulphur, a quantity of the heat is rendered latent and converted into energy, which keeps the sulphur in the liquid form; on the further application of heat to the melted sulphur until it boils, more heat is rendered latent, in order to convert the liquid sulphur into the gaseous or vaporous form. To condense the sulphur vapour to a liquid, part of the latent heat must be abstracted by bringing the vapour into contact with some cool substance, which withdraws some of the latent heat by transforming it into sensible heat; the sulphur vapour, having now lost the force or energy which kept it in the gaseous form, condenses to a liquid; if the latent heat of this liquid be in its turn abstracted by further cooling, the melted sulphur will solidify.

The subject of *latent heat* will be rendered more intelligible by quoting an example: the conversion of ice into water will be taken. If one pound of ice at 0° C. be mixed with one pound of water at 79° C., two pounds of water at 0° C. will be the result. In this case the heat which had raised one pound of water through 79° C. has disappeared, but it is not lost; it has converted the pound of ice into a pound of water, and in doing so the heat has been rendered latent by the melting ice; it has not raised the temperature of the ice, but has changed it from the solid to the liquid state; if the water be frozen, this latent heat would be transformed into, and given forth in the form of, sensible heat.

Mixtures and chemical compounds.—Before treating of the force known as chemical attraction, or chemical affinity, as it is sometimes termed, it will be well for the student to clearly understand the difference between a mixture of substances and a chemical compound. **A mixture** possesses all the properties of its ingredients, and these ingredients can be mixed in any proportions. **A chemical compound** possesses entirely different properties to those of its ingredients, and the proportion of each of its constituents is fixed and invariable. A very good example, illustrative of these two definitions, is furnished by a mixture of iron and sulphur, and by sulphide of iron, a chemical compound of iron and sulphur. If iron filings and powdered sulphur be rubbed together, it will be found that the mixture possesses all the properties of its constituents unaltered; for with a magnet the iron filings can be picked out and the sulphur left; or, by treating the mixture with a liquid called bisulphide of carbon, the sulphur can be dissolved out and the iron filings left; on evaporating the bisulphide of carbon solution, the sulphur will be left. But if the iron filings and sulphur be heated in a crucible, chemical combination takes place, and a black mass of sulphide of iron is formed, which chemical compound possesses entirely different properties to those of its constituents. A magnet is now incapable of abstracting the iron from it; bisulphide of carbon will not dissolve out the sulphur from it; on treating it with dilute sulphuric acid, a gas, called sulphuretted hydrogen, possessing an offensive odour, is evolved; neither iron nor sulphur possesses the property alone of evolving this gas when treated with dilute sulphuric acid. As may be readily comprehended, a mixture of iron filings and sulphur could be made with any proportions of the constituents, whereas the chemical compound sulphide of iron requires the constituents to be present in the fixed proportions of 56 parts by weight of iron to 32 parts by weight of sulphur. (The student will shortly learn that these are the atomic weights of iron and sulphur.) If different proportions to these are used, then a mixture of sulphide of iron with excess of either iron or sulphur will be the result, accordingly as excess of iron or sulphur has been used.

Characters of chemical attraction.—It is
3. necessary that the student should pay great attention
to the peculiar characters by which the force of
chemical attraction may be recognised, for it is by means of this force that the comparatively few elementary bodies arrange themselves into the numberless compounds of which the animal, vegetable, and mineral kingdoms are composed.

Chemical attraction is an extremely powerful
force, which acts only on the smallest particles of ①
matter, and between inappreciable distances, and, as ②
a rule, one at least of the substances must be a liquid
or a gas. An example of the last-mentioned fact is ③
obtained by powdering and rubbing together in a mortar tartaric acid and carbonate of soda; no change whatever occurs; but if water be now added to the mixture in the mortar, the two substances will dissolve, and in the dissolved state will come sufficiently close to one another to react, chemical action being manifested by the effervescence that takes place, due to the tartaric acid acting on the

carbonate of soda, forming tartrate of soda, and liberating carbonic acid gas.

Chemical attraction exists between the particles 4 of dissimilar kinds of matter, and the result of chemical combination is an entire change of properties in the compound produced. For instance: a piece of iron shows no desire to chemically unite with another piece of iron; but if the iron be heated with a dissimilar substance, as sulphur, chemical combination then takes place, and a new body—sulphide of iron—is formed, which possesses entirely different properties to those of its constituents, as has been previously explained.

A most important phenomenon, which is always the result of chemical combination, is the production of heat. It must be carefully borne in mind that 5 *whenever chemical combination takes place heat is produced or absorbed*: when heat is evolved the compound is called an *exothermic* body; if heat is absorbed an *endothermic* substance is produced. The following are a few examples of heat produced by chemical action:—

If a piece of the metal potassium be thrown upon 1 water, the potassium decomposes the water, forming hydrate of potassium, and evolving part of the hydrogen of the water; the heat produced by this chemical action is sufficient to set fire to the escaping hydrogen, which burns with a violet-coloured flame (the colour being due to a trace of potassium volatilised by the heat). If a small piece of dry phosphorus be placed on a fragment of iodine, the two substances 2 will immediately commence to combine and form iodide of phosphorus, and the heat, produced by this chemical combination, ignites that portion of the phosphorus which has not already united with the iodine. The lime-light affords another good illustration of heat produced by chemical action; to produce the light, the oxy-hydrogen flame is made to impinge on a piece of lime; the oxygen and hydrogen in combining chemically with each other produce an intense heat, and this raises the particles of the lime, upon which the flame impinges, to a white heat; the particles of lime, glowing at this white heat, emit the dazzling light.

Another, and a still more common, example of heat produced by chemical action is that derived from the 4. burning of coals in our fire-grates; in this case the constituents of the coal combine chemically with the oxygen of the air, the heat resulting from this chemical action causes the coals to glow, and inflames the gases escaping from the burning coal. In fact, in most cases where heat is obtained artificially, it is the result of chemical action.

One last important example of heat produced 5. by chemical action is that of animal heat, or the heat which maintains the temperature of the living body; the oxygen of the air that we inhale is absorbed by the blood circulating through the lungs, and is then conveyed in the blood to the various tissues of the body, where the carbon and hydrogen of the tissues become oxidised, or burnt, by this oxygen to carbonic acid gas and water respectively, and it is the heat produced by this chemical action—by this oxidation—which serves to maintain the temperature of the animal body.

As examples of endothermic substances the following may be quoted: Peroxide of hydrogen, hydrogen iodide, nitrous oxide, etc. At extremely low temperatures (— 180°) chemical action seems almost to cease.

E.G. . .
Jn. 5.

CHAPTER II.

Elements — Metals — Non-metals — Symbols — Atomic Theory — Atoms — Molecules — Atomic Weights — Laws of Chemical Combination — Quantivalence or Atomicity — Change or Variation of Quantivalence.

ELEMENTS AND COMPOUNDS.

CHEMISTRY is the science that concerns itself with the *changes* of matter and teaches us how to resolve complex forms of matter into simpler or elementary forms, and to construct compound forms of matter from the simpler or elementary forms. The resolution of complex bodies into simpler or elementary bodies is called **analysis** (ἀνά, up; λύσις, separation); and the construction of compounds from simpler bodies is called **synthesis** (σύν, together; θέσις, placing).

The numberless compounds met with in the animal, vegetable, and mineral kingdoms can all be resolved or split up by analysis, or otherwise, into about 70 seventy simpler forms of matter, which are called the *elements;* of these seventy elements, only about forty are of medical interest. 4 An **element** is a body (it may be a solid, a liquid, or a gas) that hitherto has resisted all attempts to decompose it into any simpler forms of matter; for example, silver and oxygen are two of the elements, and all attempts have, up to the present time, been incapable of decomposing them into simpler bodies. A **compound** is a body composed of two or more elements, and is therefore capable of being split up into them; for example, oxide of silver is a compound, for it is possible, by simply heating it, to resolve it into the two elements

70 Elements — 16 non metal

silver and oxygen, the former being left as finely-divided metal, and the latter escaping as a gas.

The following is a list of the elements, arranged alphabetically; classified lists of the more important elements as they are to be learnt and remembered by the student will be given shortly:—

LIST OF THE ELEMENTS.

Aluminium
Antimony
Argon*
Arsenic
Barium
Beryllium (Be)
Bismuth
Boron*
Bromine*
Cadmium (Cd)
Cæsium (Cs)
Calcium
Carbon*
Cerium (Ce)
Chlorine*
Chromium
Cobalt
Copper
Erbium (Er)
Fluorine*
Gallium (Ga)
Germanium (Ge)
Gold
Helium*
Hydrogen*
Indium (In)
Iodine*
Iridium (Ir)
Iron
Lanthanum (La)
Lead
Lithium
Magnesium
Manganese
Mercury
Molybdenum (Mo)
Nickel
Niobium (Nb)
Nitrogen*
Osmium (Os)
Oxygen*
Palladium (Pd)
Phosphorus*
Platinum (Pt)
Potassium
Rhodium (Rh)
Rubidium (Rb)
Ruthenium (Ru)
Scandium (Sc)
Selenium* (Se)
Silicon*
Silver
Sodium
Strontium
Sulphur*
Tantalum (Ta)
Tellurium* (Te)
Terbium (Tb)
Thallium (Tl)
Thorium (Th)
Tin
Titanium (Ti)
Tungsten (W)
Uranium (U)
Vanadium (V)
Ytterbium (Yb)
Yttrium (Y)
Zinc
Zirconium (Zr)

The elements are divided into two classes: viz. metals and non-metals. Sixteen non-metallic elements exist; they are distinguished in the above list by having asterisks attached to their names.

Metals and non-metals.—In much about the same way that all living things are divided into two great kingdoms, the animal and the vegetable, so the elements are divided into two classes, metals and non-metals; and just as no single character will distinguish every member of the animal kingdom from every member of the vegetable kingdom, so no single character is sufficient to distinguish all the metals from all the non-metals; for the two classes of elements gradually merge into and blend with one another, and only the far-separated members of the two classes possess any well-marked distinguishing characters. A few of the best-marked characters, and those that may be most readily recognised, are the following:—

Metals possess, or can be made to possess by polishing or by powerful compression, a peculiar surface, ① known as *metallic lustre*—a property that is well known to everyone. It is true that metals in a fine state of division, such as the reduced iron of the British Pharmacopœia, do not possess this lustre, but if by powerful pressure or hammering they are compressed into a mass, and this mass be polished, the metallic lustre is then developed. There are two of the common metals which are coloured: viz. **copper,** which is of a reddish colour, and **gold,** which is of a yellow colour. Non-metals are destitute of the peculiar surface known as metallic lustre; it is impossible to develop a mirror-like surface on a stick of phosphorus or on a piece of sulphur; the only non-metallic elements that possess anything like a metallic lustre are *iodine* and *carbon* (in the form of graphite). Metals are also good conductors of both heat and ② electricity, whereas non-metals are extremely bad conductors of these two forces. The oxides of the metals as a rule form bases, those of the non-metals ③ acids.

high Sp Gr - metals low sp gr = non-metals.

Physical conditions of the elements.—Of all the elements, seven only are gases: viz. *hydrogen*, 7 gases *oxygen*, *nitrogen*, *chlorine*, *fluorine*, *helium*, and 2 liq. *argon*. Two of the elements, *mercury* and *bromine*, are liquid at ordinary temperatures; the remaining r. n. S elements are solids. The physical condition of any element can, however, be altered: for instance, the elementary gases can be liquefied by subjecting them to powerful pressure and extreme cold; the feat of condensing oxygen and nitrogen to liquids was accomplished in the latter part of 1877 by Cailletet and by Pictet, these gases having up to that time resisted all attempts to liquefy them. Hydrogen has been liquefied by Olszewski and by Dewar. The two liquid elements, mercury and bromine, can in their turn have their physical condition altered; thus, on boiling them they become converted into vapours or gases, and by exposing them to sufficiently low degrees of cold, they freeze, or assume the solid state (for instance, mercury frequently freezes in Arctic regions). Most of the solid elements undergo an alteration of state on the application of heat: for instance, the metals when heated melt or liquefy, and on the further application of an intense heat volatilise or form vapours.

SYMBOLS.

A **symbol** is a shorthand method of representing an element. The symbol of an element consists of one or two letters, derived generally from the Latin name of the element (the symbols for potassium and sodium are derived from Arabic words). When the symbol is composed of one letter only, that letter is the first one that occurs in the name (*e.g.* the symbol for hydrogen is H, for oxygen O, for nitrogen N, for carbon C); when the symbol is composed of two letters, the first letter is the first one in the name and the second is some characteristic letter in the same name (*e.g.* the symbol for chlorine is Cl, for magnesium Mg, for platinum Pt). In most cases the Latin names are the same as the English, but in a few cases they are not, and these exceptions must be well learnt in order to remember the symbols derived from them. The following is a list of those elements whose Latin names differ from their English ones; the symbols derived from these Latin names are given in the third column:—

English Names.	Latin Names.	Symbols.
Antimony	Stibium	Sb
Copper	Cuprum	Cu
Gold	Aurum	Au
Iron	Ferrum	Fe
Lead	Plumbum	Pb
Mercury	Hydrargyrum	Hg
Potassium	Kalium (Arabic name)	K
Silver	Argentum	Ag
Sodium	Natrium (Arabic name)	Na
Tin	Stannum	Sn

The following is a list of the more common elements, with their respective symbols and approximate atomic weights; an explanation of these atomic weights will shortly be given, but previous to reading that explanation it will be advisable for the student to commit to memory the atomic weights of the elements given in the list. The order in which the elements are arranged in this table is in that of their atomic weights, commencing with hydrogen, which possesses the lowest. This order greatly assists the memory, as after studying the list the student is enabled to picture mentally in what part of the list any particular element occurs, and so a clue is gained as to its atomic weight:—

Elements.	Symbols.	Atomic Weights.
Hydrogen*	H*	1
Lithium	Li	7
Boron*	B*	11

Elements.	Symbols.	Atomic Weights
Carbon*	C*	12
Nitrogen*	N*	14
Oxygen*	O*	16
Sodium	Na	23
Magnesium	Mg	24·3
Aluminium	Al	27·1
Phosphorus*	P*	31
Sulphur*	S*	32
Chlorine*	Cl*	35·5
Potassium	K	39·1
Calcium	Ca	40
Manganese	Mn	55
Iron	Fe	56
Copper	Cu	63·6
Zinc	Zn	65·4
Arsenic	As	75
Bromine*	Br*	80
Silver	Ag	108
Tin	Sn	119
Antimony	Sb	120·4
Iodine*	I*	126·8
Barium	Ba	137·4
Mercury	Hg	200
Lead	Pb	207 20
Bismuth	Bi	208·1

The elements to which asterisks are attached are the non-metallic elements.

THE ATOMIC THEORY.

The student having now become acquainted with the differences existing between elements and compounds, the next subject to be considered is the prevailing theory with regard to the constitution of matter.

It is a familiar fact that most solid substances can, by mechanical means, be reduced to an extremely fine powder, but the particles of the finest powder when viewed under the microscope are seen in the form of little masses; that is, they are still capable of further division. Now, the question that for ages has been before the minds of philosophers and chemists is—whether matter is really infinitely divisible, or whether there is a point at which the divisibility of matter ceases. The latter idea is the prevalent one, and for the exposition and adaptation of it to the laws of chemical combination we are indebted to Dalton. The atomic theory, which is known as "Dalton's atomic hypothesis," regards matter as being composed of indivisible particles, called **atoms** (the term *atom* is derived from the Greek word *ἄτομος*, indivisible). It is impossible by any means, mechanical or otherwise, so to sub-divide any body as to split it up into its constituent atoms, nor is it possible for anyone to mentally picture an atom, since it is inconsistent for the mind to conceive of anything that is incapable of further division, as the mind always invests mental images with boundaries. By assigning to each atom a relative weight as compared with the weight of other atoms, Dalton was enabled to throw great light on, and produce satisfactory reasons for, all the observed numerical laws of chemical combination (which will shortly come under our consideration).

To understand fully the matter that follows, the definitions of the two words **atom** and **molecule** must be carefully remembered. An **atom** is the smallest proportion by weight in which an element enters into, or is expelled from, a chemical compound, the smallest weight of hydrogen so entering or leaving a chemical compound being taken as unity. More briefly, an **atom** may be defined as the smallest quantity of an *element* that is capable of existing, and it is indivisible. A **molecule** (the word *molecule* means a small mass) is the smallest quantity of a body, elementary or compound, that is capable of existing *in the free state.*

In the case of three elements, a molecule consists of one atom only: viz. mercury (Hg), zinc (Zn), and cadmium (Cd); the molecules of other elements contain two or more atoms, as $H_2.O_2.Cl_2.Br_2,I_2,S_2$ (above 500°), Se_2; the only elementary bodies containing four atoms in the molecule are phosphorus and arsenic; the molecule of phosphorus is therefore represented as P_4, and that of arsenic as As_4. Ozone, which is a modified or condensed form of oxygen, contains three atoms in the molecule, and is represented as O_3. Sulphur at 500° contains six atoms in the molecule, S_6.

Compounds are formed by the union of the atoms of different elements, and the smallest possible quantity of any compound—that is, the molecule of any compound—must contain at least two different atoms. As an example of a compound, the molecule of which only contains two elementary atoms, common salt (chloride of sodium) may be taken. This compound possesses an atom of sodium and an atom of chlorine in the molecule, which is therefore represented as NaCl. The number of atoms in the molecule of a compound is unlimited, some molecules containing a very large number, as the student will notice as he proceeds with the study of Chemistry.

ATOMIC WEIGHTS.

Every element has its own atom peculiar in properties and weight. The atomic weights of the elements represent :—

1. The relative weights of the atoms (H=1).
2. The smallest quantity by weight which can enter or leave a chemical compound (the smallest quantity of Hydrogen so entering or leaving =1).
3. The specific gravity of the element in the state of gas or vapour (H=1).

④ The number obtained by dividing 6·4 by the specific heat of the element in the solid state.

(1) **Consideration of the atomic weights of the elements as their relative weights.**—It must not be supposed that the atomic weights of the elements represent any actual weights; the weights are only comparative or relative to one another. For example, if equal volumes of hydrogen and oxygen be taken at the same temperature and under the same atmospheric pressure, it will be found that the bulk of oxygen is sixteen times as heavy as the equal bulk of hydrogen. Now, hydrogen being the lightest element, it is convenient to take it as the unit of the scale, because its combining weight is smaller than that of any other element; but this is merely a matter of convenience. Taking, therefore, the atomic weight of hydrogen as 1, the relative or atomic weight of oxygen will be 16; nitrogen is fourteen times heavier than hydrogen, and therefore its atomic or relative weight is 14. One important point must be considered here and may have been noticed by the student: and that is, that in deducing the atomic weights of hydrogen and oxygen from the relative weights of equal bulks of the gases, it is apparently assumed that a volume of hydrogen gas contains just as many molecules as an equal volume of oxygen, when the two gases are measured at the same temperature and under the same atmospheric pressure; for if the equal volumes of the two gases did not contain an equal number of units, then the units of the two gases could not possess the relative weights that the equal bulks of gases bear to one another. This important point is something more than an assumption, for it admits of experimental proof; it has been investigated by Avogadro and Ampère, and the following hypothesis bears their names.

Avogadro and Ampère's hypothesis.—

Equal volumes of different gases, at equal pressures and temperatures, contain equal numbers of molecules. As proof of this hypothesis, there is the fact that all gases are equally affected in volume by variations of pressure and temperature, physical agencies such as heat and pressure not affecting the volume of molecules, but only their distance from one another. Thus the heat that is necessary to cause half a pint of oxygen to expand to one pint also causes half a pint of hydrogen to expand to just one pint; and the pressure that is necessary to compress a pint of oxygen to half a pint will also compress a pint of hydrogen to half a pint. Now it is not conceivable that the two gases could behave in such a similar manner, unless they contained equal numbers of molecules in equal bulks.

(2) **Consideration of the atomic weights of the elements as their combining weights.**—The most important fact to be remembered by the student in connection with the atomic weights of the elements is, that they represent the proportions in which the elements unite with one another to form compounds, or the proportions in which they displace one another in compounds. Thus in the case of chloride of sodium (common salt), 23 parts by weight of sodium unite with 35·5 parts by weight of chlorine, and the two elements will only unite together in these proportions. If 35·5 grains of chlorine be brought in contact with 23 grains of sodium, the two will combine and form 58·5 grains of chloride of sodium; but if more chlorine, say 50 grains, be brought in contact with 23 grains of sodium, then the 23 grains of sodium will only unite with 35·5 grains of chlorine, and 14·5 grains of chlorine (the remainder of the 50 grains) will be left in the free state. In like manner, if 35·5 grains of chlorine be brought in contact with more than 23 grains of sodium, then the 35·5 grains of

chlorine will only be capable of uniting with 23 grains of sodium, and the remainder of the sodium will be left unattacked.

It will presently be shown that two elements are capable of uniting in different proportions to form different compounds, but the student will then notice that the varying proportions in which two elements unite with one another are always expressed by simple multiples of their atomic weights.

With regard to "4," it may be remarked that the specific heats of the elements are the relative amounts of heat required to raise equal weights through 1° Cent. In 1819 Dulong and Petit discovered that by multiplying the atomic weights of the solid elements by their respective specific heats they obtained a constant product (about 6·4). Thus:

silver, 108 × 0·057 = 6·15.
tin, 118 × 0·0562 = 6·6, etc.

THE LAWS OF CHEMICAL COMBINATION.

The following are the three laws that regulate the combination of elements to form compounds:—

1st law. The same chemical compound always contains the same elements, united in the same proportions.—This law declares that a chemical compound always possesses an unvarying composition. For instance, from whatever part of the globe chloride of sodium (common salt) be obtained, or by whatever method it may be manufactured, it will always be found on analysis to contain 23 parts by weight of sodium to 35·5 parts by weight of chlorine, and these proportions will never vary in the compound. Again, if pure water be obtained from any source, and analysed, it will be found to contain 2 parts by weight of hydrogen to 16 parts by weight of oxygen, and in all samples of water these proportions are invariable.

This law, although a very simple one, is an extremely important one, for it confers on Chemistry the dignity of an exact science :—

2nd law. When two elements unite together, in different proportions, to form different compounds, they do so in simple multiples of each other.—Thus, let A and B represent two elements, the following arrangements then show how these two elements might combine in different proportions to form different compounds :—

$A + B$, $A + 2B$, $A + 3B$, $A + 4B$, etc.
Or, $2A + B$, $2A + 3B$, $2A + 5B$, $2A + 7B$, etc.
Or, $A + B$, $A + 3B$, $A + 5B$, etc.

It will be noticed that the varying combining proportions of A and B are indicated by the simple multiples 1, 2, 3, 4, etc., no halving or quartering of an elementary atom ever taking place.

The student will meet with numerous examples of this law as he proceeds with the study of Chemistry; for the present, it will be sufficient to bring before his notice a few illustrations of it in order to complete its explanation. Carbon forms with oxygen two compounds : the one containing the least oxygen is called carbonic oxide (CO), and the one containing most oxygen is called carbonic acid gas (CO_2); carbonic oxide contains by weight 12 parts of carbon to 16 of oxygen, and carbonic acid gas contains 12 parts of carbon to 32, or 16×2, of oxygen; in this case the simple multiples 1 and 2 represent the different proportions in which the two elements carbon and oxygen unite with one another.

A few examples of different compounds belonging to some of the members of the graphic representations previously given, may assist the student in understanding this law.

EXAMPLES.

2A + B ...	N_2O ...	Nitrous oxide	Three of the compounds of nitrogen and oxygen.
2A + 3B...	N_2O_3..	Nitrous anhydride	
2A + 5B...	N_2O_5...	Nitric anhydride	
A + 2B ...	SO_2 ...	Sulphurous anhydride	The two compounds of sulphur and oxygen.
A + 3B ...	SO_3 ...	Sulphuric anhydride	
A + 3B ...	PCl_3...	Phosphorus trichloride	The two compounds of phosphorus and chlorine.
A + 5B ...	PCl_5...	Phosphorus pentachloride	

This second law of chemical combination is an extremely important one, as it adds great weight to the idea of the existence of atoms; for, since an atom is supposed to be indivisible, it is easy to understand why, in cases where several compounds of the same elements exist, the increase is always in some simple multiple of the combining weight, in other words, there is no halving nor quartering of atoms; in fact, the theory of the existence of atoms is perfectly in harmony with the law of multiple proportions that has just been explained.

3rd law. The proportions in which any two elements unite with a third are the same proportions in which they unite with each other, or simple multiples of those proportions.—For example, 39 parts of potassium unite with 35·5 parts of chlorine to form chloride of potassium, and 39 parts of potassium unite with 127 parts of iodine to form iodide of potassium; therefore 35·5 parts of chlorine would unite with 127 parts of iodine to form a compound of iodine with chlorine (chloride of iodine). In this case, the proportions in which the two elements chlorine and iodine unite with the third element potassium are the same proportions in which they unite with each other.

These three laws are sometimes called respectively:

(1) The law of constant proportions.
(2) The law of multiple proportions.
(3) The law of reciprocal proportions.

The discovery of the second law, the law of multiple proportions, by Dalton in 1804, was of the highest importance; before Dalton's time the composition of a substance was expressed in percentage numbers. Thus the two oxides of carbon:

Carbonic oxide, 42·86% carbon and 57·14% oxygen.
Carbon dioxide, 27·27% carbon ,, 72·73% oxygen.

And again, two of the hydrocarbons:

Olefiant gas, 85·7% carbon and 14·3% hydrogen.
Marsh gas, 75·0% carbon ,, 25·0% hydrogen.

Dalton was apparently the first to notice that in olefiant gas *one* part of hydrogen was united to *six* parts by weight of carbon, and that in marsh gas *two* of hydrogen were united to *six* parts of carbon, and *to appreciate the importance of this fact.* Again, in carbonic oxide 6 parts of carbon unite with 8 of oxygen, and in carbon dioxide 6 parts of carbon unite with 16 of oxygen. This he explained by assuming that the (relative) weight of the carbon atom was 6, and that of the oxygen atom was 8, and that in carbonic oxide we had 1 atom of each element present, and in the dioxide 1 atom of carbon to 2 atoms of oxygen, which facts could be easily symbolised by the formulæ CO and CO_2. (For reasons given in subsequent pages the above atomic weights have been doubled.)

CLASSIFICATION OF THE COMMONER ELEMENTS ACCORDING TO THEIR QUANTIVALENCE IN ORDINARY COMPOUNDS.

Univalents or Monads.	Bivalents or Dyads.	Trivalents or Triads.	Quadrivalents or Tetrads.	Quinquivalents or Pentads.	Sexivalents or Hexads.
Hydrogen ...H	Oxygen ......O	Aluminium..Al	Carbon C	Nitrogen ...N	Sulphur......S
Chlorine Cl	Barium ......Ba	Boron.........B	Silicon ......Si	Phosphorus P	Chromium...Cr
Bromine ......Br	Calcium ......Ca	Iron ....Fe	Tin ....Sn	Arsenicum...As	Manganese Mn
Iodine I	Strontium ...Sr	Gold ....Au	Platinum ...Pt	Antimony ...Sb	
Fluorine ......F	Magnesium..Mg	Bismuth ...Bi	*Sulphur**......S		
Potassium ...K	Zinc ....Zn	*Nitrogen** ...N	*Chromium**...Cr		
Sodium ......Na	Copper ......Cu	*Phosphorus** P	*Manganese**...Mn		
Lithium Li	Lead ....Pb	*Arsenic** ...As			
Silver ....Ag	Mercury ...Hg	*Antimony**...Sb			
*Nitrogen** ...N	Cadmium ...Cd				
	*Sulphur** ...S				
	*Chromium**...Cr				
	*Manganese**..Mn				
	*Carbon** C				
	*Iron** ....Fe (in ferrous salts).				
	*Tin** ....Sn (in stannous salts).				

* *See* page 26.

QUANTIVALENCE, ATOMICITY, OR VALENCY.

By the quantivalence or atomicity of an element is meant its atom-fixing power: that is, the equivalent or saturating value possessed by the atom of an element, represented by the number of atoms of hydrogen to which it is equivalent. Thus, chlorine combines with but one atom of hydrogen, as in HCl; oxygen combines with two atoms of hydrogen, as in H_2O; nitrogen with three, NH_3; carbon with four, CH_4, etc.

Any dyad or bivalent element possesses twice the atom-fixing power of a monad or univalent element. A triad or trivalent element possesses three times the atom-fixing power of a monad element, so that one atom of a triad will combine with and saturate three atoms of a monad. *Example.*—Chloride of bismuth ($BiCl_3$) consists of one atom of the triad element bismuth united with three atoms of the monad element chlorine.

The combination of a dyad with a triad does not at first seem so easy, but bearing in mind that a triad possesses an atom-fixing power represented by three, as compared with a dyad, which possesses an atom-fixing power represented by two, evidently, then, two atoms of a triad will unite with and satisfy three atoms of a dyad, for they will then both possess an equal atom-fixing power, represented by six; just as two threepenny pieces would be equal in value to three twopenny pieces. *Example.*—Oxide of bismuth (Bi_2O_3) consists of two atoms of the triad bismuth united with three atoms of the dyad oxygen.

One atom of a tetrad or quadrivalent element will combine with and saturate four atoms of a univalent element, or two atoms of a dyad or bivalent element. *Examples.*—Perchloride of platinum ($PtCl_4$) consists of one atom of the tetrad platinum united with four atoms of the monad chlorine. Carbonic acid gas (CO_2) consists of one atom of the tetrad carbon united with two atoms of the dyad oxygen.

One atom of a pentad or quinquivalent element is capable of uniting with and saturating five atoms of a monad or univalent element. *Example.*—Pentachloride of phosphorus (PCl_5) consists of one atom of the pentad phosphorus united with five atoms of the monad chlorine. When a pentad unites with a dyad, two atoms of the pentad will satisfy and saturate five atoms of the dyad, for two atoms of a pentad will possess an atom-fixing power equal to five atoms of a dyad, since they will then both possess an equal atom-fixing power, represented by ten, just as two fivepenny pieces would be equal in value to five twopenny pieces. *Example.*—Phosphoric anhydride (P_2O_5) consists of two atoms of the pentad phosphorus united with five atoms of the dyad oxygen.

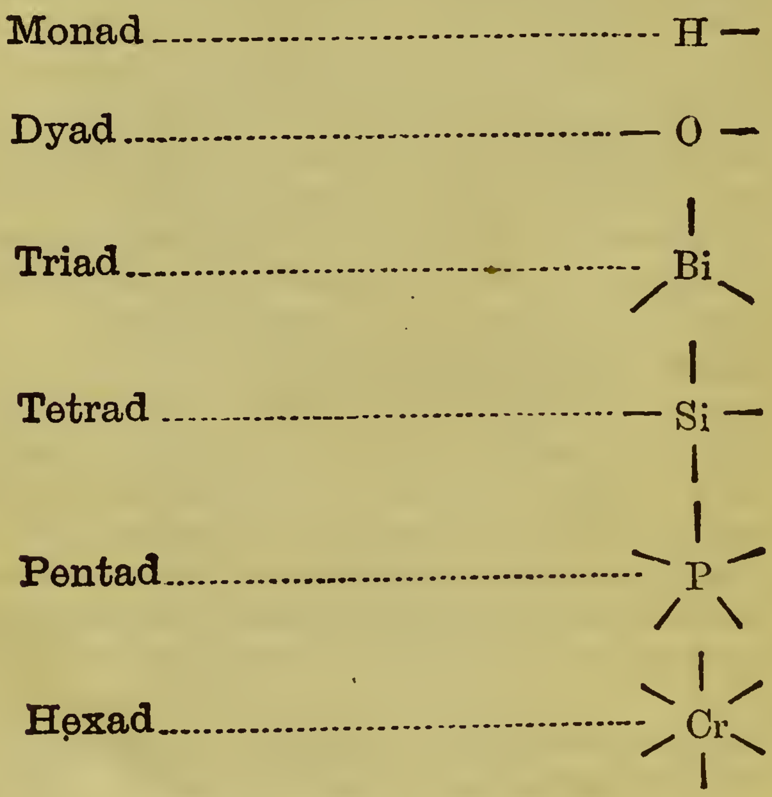
Lastly, a hexad or sexivalent element is one that possesses six times the atom-fixing power of a monad or univalent element, or three times the atom-fixing power of a dyad, and so on. *Examples.*—Fluoride of chromium (CrF_6) consists of one atom of the hexad chromium united with six atoms of the monad fluorine. Chromic anhydride (CrO_3) consists of one atom of the hexad chromium united with three atoms of the dyad oxygen.

The quantivalence or atomicity of an element is sometimes represented by small dashes or by Roman numerals placed over its symbol, thus:

Monad or univalent	H^{i}
Dyad or bivalent	O^{ii}
Triad or trivalent	Bi^{iii}
Tetrad or quadrivalent	Si^{v}
Pentad or quinquivalent	P^{v}
Hexad or sexivalent	Cr^{vi}

GRAPHIC REPRESENTATION OF THE QUANTIVALENCE OR ATOMICITY OF THE ELEMENTS.

The quantivalence of an element may be represented graphically by fixing to its symbol lines corresponding in number to the degree of its atom-fixing power. A monad is represented as possessing one arm, a dyad as possessing two arms, a triad as possessing three arms, and so on; thus:



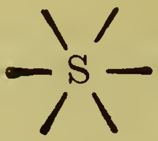
It is scarcely necessary to caution the student against supposing that elements actually have arms projecting from them; all that we know is that such an element as oxygen possesses twice the atom-fixing power of hydrogen, and the graphic symbols serve the purpose of showing how one atom of oxygen is capable of uniting with two atoms of hydrogen; they represent in a manner that at once appeals to the mind of the student how different elements are capable of exerting different atom-fixing powers. These hypothetical arms are generally spoken of and written of as "bonds," but the term "bond" is open to some objection, and the better and less objectionable term "affinity" will therefore be used in this book. Thus, a monad possesses one affinity, a dyad two affinities, a triad three affinities, and so on.

Change or variation of quantivalence.—It will be noticed in the table of the elements arranged according to quantivalence on page 23, that frequently an element is inserted in more than one column, that is, apparently possesses more than one quantivalence; an explanation of the reason why an element is capable of exerting different atom-fixing powers will now be given. It should be noticed in the table referred to, that when an element is not exerting its full quantivalence, it is distinguished by being printed in italics and by having an asterisk attached to its name.

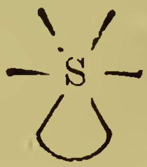
The commoner elements that possess varying quantivalences are:

Sulphur, which acts as a *hexad*, *tetrad*, and *dyad*.
Chromium ,, ,, ,, ,,
Manganese ,, ,, ,, ,,
Nitrogen, which acts as a *pentad*, *triad*, and *monad*.
Phosphorus, which acts as a *pentad* and *triad*.
Arsenic ,, ,, ,, ,,
Antimony ,, ,, ,, ,,
Carbon, which acts as a *tetrad* and *dyad*.
Iron ,, ,, *triad* ,,
Tin ,, ,, *tetrad* ,,

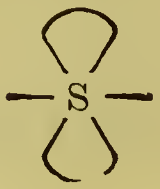
As an example of the first group, the members of which can act as hexads, tetrads, or dyads, we will take sulphur. The sulphur atom as a hexad is represented graphically as possessing six affinities, thus:



Now, supposing two of the six affinities cease to exert their atom-fixing power, which can be imagined by supposing a pair of affinities to grasp one another and so neutralise their fixing powers, the sulphur atom will then only be exerting an atom-fixing power represented by four, and will therefore be acting as a tetrad. The sulphur atom in this condition is represented graphically thus :



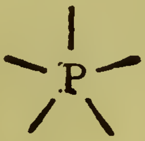
Again, suppose two pairs of affinities to grasp or neutralise one another, the sulphur atom will then only have two affinities capable of exerting a uniting or combining power, and will therefore be acting as a dyad or bivalent. The sulphur atom in this condition is represented graphically thus :

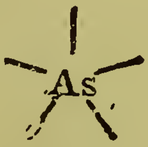


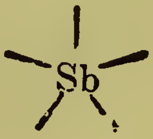
For instance, in sulphuric anhydride ($S^{vi}O^{ii}_3$) the sulphur is exerting its full *sexivalent* atomicity ; in sulphurous anhydride ($S^{iv}O^{ii}_2$) the sulphur is only exerting *quadrivalent* atomicity ; in sulphuretted hydrogen ($H^{i}_2S^{ii}$) the sulphur is only exerting *bivalent* atomicity.

When two affinities neutralise one another, the act is spoken of as a pair of affinities becoming latent; that is, the combining power is not destroyed, but is simply rendered latent or is hidden for the time, for it is possible, by chemical means, to compel these pairs of latent affinities to unloose themselves and to exert their full atom-fixing power. Thus, as the student will learn later, it is possible to compel the S in H_2S, in which it is acting as a dyad, to unloose H_2S a pair of its latent affinities and act as a tetrad, and, in like manner, sulphur exerting the atomicity of a tetrad can be made to exert its full atom-fixing power as a hexad, by the opening of its last pair of latent affinities.

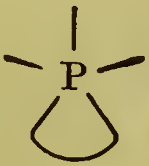
In a similar way the three elements, phosphorus, arsenic, and antimony, are capable of acting as pentads and triads. The atoms of these three elements when they act as pentads are represented graphically thus:

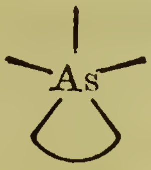


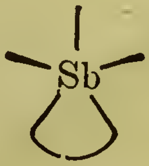




When acting as triads, or only exerting trivalent atomicity, a pair of affinities become latent, and the atoms of the three elements would then be represented graphically thus:







For instance, in phosphoric anhydride ($P_2^{v}O_5^{ii}$) the phosphorus is exerting its full power as a *pentad* or *quinquivalent*; in phosphorous anhydride ($P_4^{iii}O_6^{ii}$) the phosphorus is only exerting the power of a *triad* or *trivalent.*

In arsenic anhydride ($As_2^{v}O_5^{ii}$) the arsenic is exerting its full power as a *pentad* or *quinquivalent ;* in arsenious anhydride ($As_4^{iii}O_6^{ii}$) the arsenic is only exerting the power of a *triad* or *trivalent.*

In pentachloride of antimony ($Sb^{v}Cl_5^{i}$) the antimony is exerting its full power as a *pentad* or *quinquivalent ;* in the trichloride of antimony ($Sb^{iii}Cl_3^{i}$) the antimony is only exerting the power of a *triad* or *trivalent.*

There are certain anomalies with regard to the valency of the elements nitrogen and iron which await future explanation. Thus nitrogen in most of its compounds is an element whose valency is odd, but in nitric oxide (NO) it is apparently a dyad. Iron in ferrous oxide (FeO) is a dyad, but in ferric chloride ($FeCl_3$) it seems to be trivalent.

The elements whose valency is represented by odd numbers (1, 3, 5, etc.) are sometimes called *perissads,* those with even numbers (2, 4, 6) *artiads*

rissads
onads
riads
intads

Artiads
Dyads.
Tetrads
Hexads

CHAPTER III.

Acidulous Radicles—Elementary Radicles—Compound Radicles—Quantivalence of Acidulous Radicles—Acids—Bases—Salts.

ACIDULOUS RADICLES.

THE term *radicle* signifies an unsaturated element or group of elements. An *acidulous* radicle is an element or group of elements which are electro-negative, *i.e.* they are liberated or tend to be liberated at the positive electrode when their compounds are decomposed by the passage of a current of electricity. Thus Cl, Br, I, etc., are elementary acidulous radicles; NO_3, SO_4, etc., are acidulous compound radicles.

A *compound radicle* may be defined as a group of elements which plays the part of one element, and which passes through many reactions without being decomposed into its constituent elements. Thus the group NH_4 is found in all the ammonium salts, NH_4Cl, $(NH_4)_2SO_4$. The group SO_3 in all the sulphites, Na_2SO_3, $CaSO_3$, etc.

These compound radicles may be monovalent, divalent, etc., according to their degree of unsaturation.

We will now take a few examples, and show by graphic representations that it is the degree of unsaturation of a radicle (simple or compound) that determines its quantivalence or atom-fixing power.

1. As examples of univalent acidulous radicles, we will select the radicles of

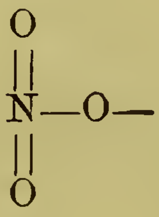
(*a*) Chlorides	Cl^{i}
(*b*) Nitrates	NO_3^{i}
(*c*) Nitrites	NO_2^{i}
(*d*) Cyanides	CN^{i}

(*a*) The radicle of chlorides (Cl) is the atom of the element chlorine, which being a univalent element has, therefore, a combining power represented by one.

Cl—

Graphic representation of the radicle of chlorides.

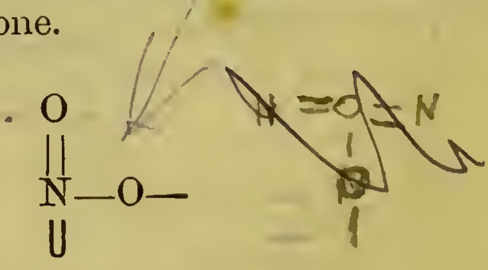
(*b*) The radicle of nitrates ($N^{v}O_3^{ii}$) consists of three bivalent oxygen atoms united with one quinquivalent nitrogen atom; the five affinities of the nitrogen atom would therefore be capable of combining with five out of the six affinities of the three oxygen atoms, leaving one affinity unsaturated, and therefore constituting the radicle a univalent one.



$$\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{N}}{-}O{-}$$

Graphic representation of the radicle of nitrates.

(*c*) In the radicle of nitrites ($N^{iii}O_2^{ii}$) the nitrogen is only exerting trivalent atomicity (a pair of its affinities being latent), and is united with two bivalent oxygen atoms; the three free affinities of the nitrogen atom will therefore saturate three out of the four affinities of the two oxygen atoms, leaving one affinity unsaturated, and therefore constituting the radicle a univalent one.



$$\overset{\overset{\displaystyle O}{\|}}{\underset{\displaystyle U}{N}}{-}O{-}$$

Graphic representation of the radicle of nitrites.

(*d*) In the radicle of cyanides ($C^{iv}N^{v}$) an atom of the quadrivalent element carbon is united with an atom of the quinquivalent element nitrogen, leaving one affinity unsaturated, and so constituting the radicle a univalent one. This radicle can also be graphically represented by making the nitrogen trivalent, when one of the affinities of the carbon is left unsaturated.

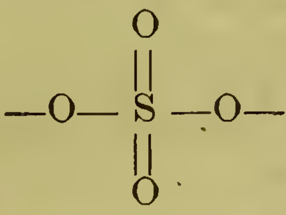
$$C\equiv N- \qquad\qquad -C\equiv N\supset$$

Graphic representations of the radicle of cyanides.

2. As examples of bivalent acidulous radicles we will take the radicles of

Sulphate ... ... $S^{vi}O^{ii}_4$

In the radicle of sulphates ($S^{vi}O^{ii}_4$), one atom of sulphur which is exerting its full sexivalent atomicity is united with four atoms of the bivalent oxygen; the six affinities of the sulphur atom will satisfy or combine with six out of the eight affinities of the four oxygen atoms, leaving two affinities unsaturated, and therefore constituting the radicle a bivalent one.



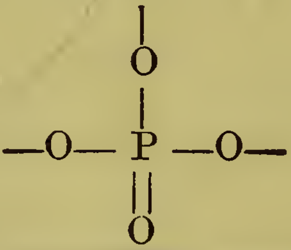
$$\begin{array}{c} O \\ \| \\ -O-\ S\ -O- \\ \| \\ O \end{array}$$

Graphic representation of the radicle of sulphates.

3. As examples of trivalent acidulous radicles we will take the radicles of

Phosphates ... ... $P^{v}O^{ii}_4$

The radicle of phosphates ($P^{v}O^{ii}_4$) is composed of one quinquivalent phosphorus atom united with four bivalent oxygen atoms; the five affinities of the phosphorus atom will satisfy or combine with five out of the eight affinities of the four oxygen atoms, leaving three affinities unsaturated, and therefore constituting the radicle a trivalent one.



$$-O-\overset{\overset{|}{O}}{\underset{\underset{O}{\|}}{P}}-O-$$

Graphic representation of the radicle of phosphates.

These examples will be quite sufficient to enable the student to comprehend that the quantivalence of a radicle is represented by the extent to which it is unsaturated, and the graphic representations will teach how it is that a certain radicle possesses a certain quantivalence; graphic representations of the more complex acidulous radicles (*e.g.* of acetates $C_2H_3O_2$, or of tartrates $C_4H_4O_6$) have not been given, as they would be of no assistance at present to the student in that part of the subject which we are now dealing with.

We will now give a list of the more important acidulous radicles, arranged in groups according to their quantivalence:

UNIVALENT ACIDULOUS RADICLES.

Name.	Formula.
Radicle of Chlorides	Cl
,, Iodides	I
,, Bromides	Br
,, Fluorides	F
,, Cyanides	CN or Cy
,, Cyanates	CNO or CyO

UNIVALENT ACIDULOUS RADICLES (*contd.*).

Name.	Formula.
Radicle of Hypochlorites	ClO
„ Nitrites	NO_2
„ Nitrates	NO_3
„ Chlorates	ClO_3
„ Iodates	IO_3
„ Bromates	BrO_3
„ Formates	CHO_2
„ Acetates	$C_2H_3O_2$

BIVALENT ACIDULOUS RADICLES.

Name.	Formula
Radicle of Sulphites	SO_3
„ Sulphates	SO_4
„ Chromates	CrO_4
„ Carbonates	CO_3
„ Oxalates	C_2O_4
„ Tartrates	$C_4H_4O_6$

TRIVALENT ACIDULOUS RADICLES.

Name.	Formula.
Radicle of Borates	BO_3
„ Arsenites	AsO_8
„ Arseniates	AsO_4
„ Phosphates	PO_4
„ Citrates	$C_6H_5O_7$

QUADRIVALENT ACIDULOUS RADICLES.

Name.	Formula.
Radicle of Silicates	SiO_4
„ Ferrocyanides	FeC_6N_6 or $FeCy_6$

The formulæ of these acid radicles and their quantivalences, together with the symbols of the elements and their atomicities (*see* list on page 23), must be thoroughly committed to memory; the student will then be able easily to construct a formula, and, knowing how to construct formulæ, the representation of chemical reactions by means of equations is but another step forward. Before dealing with the construction of formulæ and equations, it will be as well, at this stage of the work, to introduce to the notice of the student three most important classes of bodies, viz. **acids, bases,** and **salts.**

Acids are bodies that always contain hydrogen, which hydrogen is capable of being partially or entirely displaced by a metal, to form a salt; in fact, the combination of any one of the acidulous radicles with its equivalent quantity of hydrogen, forms an acid. Acids that contain one atom of displaceable hydrogen are called *monobasic;* those containing two atoms of displaceable hydrogen, *dibasic;* those containing three atoms of displaceable hydrogen, *tribasic;* and so on. Thus nitric acid ($H^{i}NO_3^{i}$), which is composed of the univalent nitric radicle united with one atom of hydrogen, is an example of a *monobasic acid;* sulphuric acid ($H_2^{i}SO_4^{ii}$), which is composed of the bivalent sulphuric radicle united with two atoms of hydrogen, is an example of a *dibasic acid;* phosphoric acid ($H_3^{i}PO_4^{iii}$), which is composed of the trivalent phosphoric radicle united with three atoms of hydrogen, is an example of a *tribasic acid.* It should be carefully remembered that when the term "acid" is applied to a body destitute of hydrogen, the term is erroneously employed; for example, the so-called "arsenious acid" (As_4O_6) of the British Pharmacopœia cannot be an acid, for it contains no hydrogen; it is the anhydride of arsenious acid, an *anhydride* being derived from an acid by the abstraction of the elements of water. Two distinguishing characters possessed by most acids are a sour taste and the property of changing the colour of blue litmus paper to red.

Bases are bodies that are capable of combining with acids to form salts. Bases sometimes possess a caustic or alkaline taste, and have the property of changing the colour of red litmus paper to blue. The term base has been applied to three classes of substances :

(i) **Oxides,** of which lime, or oxide of calcium (CaO), and magnesia, or oxide of magnesium (MgO), may be mentioned as examples.

(ii) **Hydrates,** of which caustic potash, or hydrate of potassium (KHO), and slaked lime, or hydrate of calcium ($Ca2HO$), may be mentioned as examples.

(iii) A class of bodies such as ammonia gas (NH_3) and its organic derivatives, the amines, etc.

Salts are the compounds resulting from the action of a base on an acid ; an *acid salt* is obtained by the partial neutralisation of an acid by a base, so that its properties are partly those of an acid and partly those of a salt ; as $HKSO_4$, acid potassium sulphate.

When *all* the hydrogen of the acid is replaced by a metal the salt is called *normal or neutral*, as K_2SO_4, neutral potassium sulphate. A *basic salt* may be considered as derived from the hydroxide or hydrate of a metal, in which *all* the hydroxyl has not been replaced by the acid radicle. Thus, bismuth hydroxide $Bi(HO)_3$; if all the HO is replaced, we have the neutral bismuth nitrate $Bi(NO_3)_3$; if part only is replaced we have basic nitrates, $BiHO(NO_3)_2$ and $Bi(HO)_2NO_3$.

CHAPTER IV.

Formulæ—Construction of Formulæ—Molecules and Molecular Weights—Specific Gravities of Gases and Vapours—Atomic Weight, Molecular Weight, Equivalent Weight—Uses of Terminations.

FORMULÆ.

A **formula** is a representation of the composition of a body by means of symbols, which may be regarded as chemical shorthand; it consists of a grouping of the symbols of the elements composing the body, with numbers attached to these symbols indicating the proportions in which the elements occur in the body; when no number is attached to the symbol of an element, the number one is understood. We will now show, by a few examples, how to construct the formulæ of acids and salts.

An **acid** is simply a compound of an acidulous radicle with hydrogen. Hydrogen being a univalent element, a univalent acidulous radicle will unite with and be saturated by, one atom of hydrogen; thus:

$H^{i}Cl^{i}$ is the formula of hydrochloric acid.
$H^{i}NO_3^{i}$,, ,, nitric acid.
$H^{i}C_2H_3O_2^{i}$,, ,, acetic acid.

A bivalent acidulous radicle will require two atoms of the univalent hydrogen to saturate it; thus:

$H_2^{i}SO_4^{ii}$ is the formula of sulphuric acid.
$H_2^{i}C_2O_4^{ii}$,, ,, oxalic acid.
$H_2^{i}C_4H_4O_6^{ii}$,, ,, tartaric acid.

A trivalent acidulous radicle will, in its turn, require three atoms of hydrogen to saturate it and form an acid; thus:

$H_3^{i}BO_3^{iii}$ is the formula of boracic acid.
$H_3^{i}PO_4^{iii}$,, ,, phosphoric acid.
$H_3^{i}C_6H_5O_7^{iii}$,, ,, citric acid.

A quadrivalent acidulous radicle will require four atoms of hydrogen to saturate it and form an acid; thus:

$H_4^{i}SiO_4^{iv}$ is the formula of silicic acid.
$H_4^{i}FeC_6N_6^{iv}$,, ,, hydroferrocyanic acid.

The student can therefore construct the formula of any acid by remembering the formula and quantivalence of the acidulous radicle of that acid, and then uniting the radicle with its equivalent number of hydrogen atoms.

The construction of the formulæ of **salts** is as easy as that of acids, though some of them may appear, at first, more complex. We will first consider the formulæ of salts containing univalent acidulous radicles.

Chloride of sodium is formed by the union of the univalent element sodium with the univalent radicle chlorine; its formula is therefore

$$Na^{i}Cl^{i}.$$

In the case of chloride of barium, two equivalents of the univalent radicle chlorine will be required to satisfy the bivalent metal barium; the formula is therefore:

$$Ba^{ii}Cl_2^{i}.$$

Nitrate of bismuth will require three equivalents of the univalent nitric radicle to satisfy one equivalent of the trivalent metal bismuth; its formula is therefore:

$$Bi^{iii}(NO_3)^{i}_{3}.$$

Chloride of platinum will require four equivalents of the univalent radicle chlorine to satisfy one equivalent of the quadrivalent element platinum; its formula is therefore:

$$Pt^{iv}Cl^{i}_{4}.$$

We will next take a few examples of the formulæ of salts containing bivalent acidulous radicles.

Sulphate of potassium is composed of the univalent metal potassium united with the bivalent sulphuric radicle; two equivalents of the former will therefore be required to satisfy one of the latter, so that the formula is:

$$K^{i}_{2}SO^{ii}_{4}.$$

Carbonate of calcium consists of the bivalent metal calcium united with the bivalent carbonic radicle; one equivalent of each will therefore satisfy one another, so that the formula is:

$$Ca^{ii}CO^{ii}_{3}.$$

The formula of citrate of potassium requires the union of the univalent element potassium with the trivalent citric radicle; three atoms of the former will satisfy one equivalent of the latter; the formula is therefore:

$$K^{i}_{3}C_6H_5O^{iii}_{7}.$$

The formula of phosphate of calcium requires the union of the bivalent metal calcium with the trivalent phosphoric radicle. Now, three equivalents of the bivalent calcium will satisfy two equivalents of the trivalent phosphoric radicle, for they will then both possess an atom-fixing power represented by six; the formula is therefore:

$$Ca_3^{ii}(PO_4)_2^{iii}.$$

Citrate of bismuth being composed of the trivalent metal bismuth united with the trivalent citric radicle, an equivalent of each will form a saturated compound; the formula is therefore:

$$Bi^{iii}C_6H_5O_7^{iii}.$$

We will lastly give two examples of the formulæ of salts containing quadrivalent acidulous radicles.

The formula of ferrocyanide of potassium requires the union of the univalent metal potassium with the quadrivalent radicle of ferrocyanides. Evidently, four equivalents of the former will satisfy one of the latter; the formula is therefore:

$$K_4^{i}FeCy_6^{iv}.$$

Silicate of calcium is composed of the bivalent metal calcium united with the quadrivalent silicic radicle; two equivalents of the former will therefore satisfy one of the latter; the formula is therefore:

$$Ca_2^{ii}SiO_4^{iv}.$$

The student will find it good practice to write out the formulæ of the following salts, and have the results looked over by a teacher or some other competent person:—

KI Iodide of potassium.
MgBr Bromide of magnesium.
Cu(C2H3O2)2 Acetate of copper.
Chlorate of calcium.
Ca(ClO3)2 ✓

Pb(Cy)2 ✓
Cyanide of lead.
Ag2(C4 H
Tartrate of silver.
Na C
Carbonate of sodium.
Oxalate of calcium.
CaC2O4

SO_3 Sulphite of zinc.
$(C_2O_4)_3$ Oxalate of bismuth. BO_3
Borate of sodium. Na_3
PO_4 Phosphate of lead.

Citrate of magnesium. Mg
Silicate of potassium. K Si
Ferrocyanide of zinc.
Ferricyanide of lead.

On page 18, Avogadro's hypothesis was enunciated, "that equal volumes of all gases contain the same number of molecules" (at the same temperature and pressure). Some important deductions from this law will now be considered.

If we conceive a cubical box of a certain size filled with hydrogen, and a box of exactly the same size filled with chlorine, according to the above law these boxes will each contain exactly the same number of particles. Suppose the number of particles of hydrogen to be 1,000, then the number of particles of chlorine will also be 1,000. Now, if we cause these volumes of hydrogen and chlorine to combine by mixing them and exposing them to daylight we shall obtain, as a matter of fact, a volume of hydrogen chloride gas exactly double that of the hydrogen originally taken. As the volume of the hydrogen chloride is twice that of the hydrogen, it must contain twice as many particles, that is 2,000, and each and every one of these particles of HCl contains both hydrogen and chlorine, therefore there must be 2,000 particles of H and 2,000 of Cl in the 2,000 of HCl, and these were derived respectively from the 1,000 particles of *free* hydrogen and the 1,000 particles of *free* chlorine. It follows, therefore, that each particle of free hydrogen divided into two particles when it combined with the chlorine, and that each particle of free chlorine similarly divided into two when it combined with the hydrogen. The particle of free hydrogen is called a *molecule*, and the two particles into which it splits are called *atoms*, and we say that the molecule of hydrogen contains two atoms, and we write the symbol for the molecule H_2; similarly the molecule of chlorine is Cl_2. In a similar way it can be shown that the molecule of oxygen and of some other elements contains two atoms.

Another important deduction is the following :—

As equal volumes of all gases contain the same number of molecules, the weights of equal volumes of gases must be proportional to the weights of their respective molecules.

Now, we have just seen that the weight of the molecule of hydrogen is twice that of the atom ; if we assume the weight of the atom of hydrogen to be 1, the molecular weight will be 2, and if we take the specific gravity of hydrogen as our unit for the specific gravity of gases, then

$$\text{Sp. gr. of H} = \frac{\text{molecular weight}}{2}.$$

As the specific gravities of all gases are proportional to their molecular weights, the same argument holds, and so we may say that

$$\text{the sp. gr. of any gas or vapour} = \frac{\text{molecular weight}}{2},$$

$$\text{or, the molecular weight} = 2 \times \text{sp. gr. } (H = 1).$$

We thus have a means of finding the molecular weight of any substance if we can obtain it as a gas or vapour, and determine its specific gravity in that state.

The sp. gr. of O is 16, and its molecular weight 32, its atomic weight 16, and its molecule O_2, since $\frac{32}{16} = 2$.

Sp. gr. of bromine is 80, m. w. 160, Br_2.

Sp. gr. of mercury vapour is 100, m. w. 200, and as its molecular weight and atomic weight are identical, its molecule contains but one atom $\left(\frac{200}{200} = 1\right)$, and its molecule is Hg, the same as its atom

Q. 2 p. 53 16

?

In the same way the molecules of zinc, cadmium, potassium, and sodium are found to contain but one atom, Zn, Cd, K, Na.

Sp. gr. of phosphorus vapour is 62, m. w. 124, now the atomic weight is 31, and $\frac{124}{31} = 4$, therefore the molecule of phosphorus contains four atoms, P_4; in a similar way, the molecule of arsenic is found to be As_4.

Many elements, as platinum, gold, iron, etc., have not had their vapour densities satisfactorily determined, owing to the high temperature required to effect their volatilisation, and we are therefore ignorant of their molecular weights.

The following table gives a list of those elements whose vapour density has been determined, and the symbols of their molecules deduced therefrom :—

4 p.

		Sp. Gr.			Sp. Gr.
H_2	...	1	Se_2	...	79
O_2	...	16	P_4	...	62
N_2	...	14	As_4	...	150
F_2	...	19	Na_1	...	11·5
Cl_2	...	35·5	K_1	...	19·5
Br_2	...	80	Zn_1	...	32·5
I_2	...	127	Cd_1	...	56
S_6 below 500°		96	Hg_1	...	100
S_2 at 900°		32			

It will be observed that nine elements have two atoms in the molecule, five have only one, two have four, one has six; in addition, it may be mentioned that the molecule of ozone, a special form of oxygen, has three, O_3.

There is a second method of determining the molecular weights of substances, by noting the depression of the freezing point of a solvent (water, benzene or glacial acetic acid) when the substances are dissolved in it. Raoult has proved that when molecular weights of different substances are dissolved in the same amount of a solvent, they show the same depression of their freezing points. Glacial acetic acid is the solvent usually employed, and the method has been chiefly used for organic substances; when glacial acetic acid is used,

$$\text{the molecular weight} = 39 \times \frac{\text{grammes of substance in 100 grammes of solvent}}{\text{the depression in freezing point}}$$

(*see* ORGANIC CHEMISTRY, Chapter II.).

The statement that the specific gravity of a gas or vapour is one half its molecular weight, holds good for compounds as well as elements; thus the specific gravity of ammonia (NH_3) is $\frac{17}{2} = 8{\cdot}5$; of alcohol vapour (C_2H_6O), $\frac{46}{2} = 23$; of carbon dioxide (CO_2), $\frac{44}{2} = 22$. There are some *apparent* exceptions to this law in the case of ammonium chloride, calomel, etc., which will be discussed hereafter.

It will be convenient here to distinguish between atomic weight, molecular weight, and equivalent weight.

Atomic weight applies only to elements, and has already been defined and discussed on p. 16.

Molecular weight.—The molecular weight of any body (solid, liquid, or gas) is the sum of the atomic weights of the elements composing its molecule. Thus, the molecular weight of oxygen is 32.

$$O_2 = 16 \times 2 = 32.$$

The molecular weight of hydrochloric acid is 36·5.

$$\begin{array}{rl} H = & 1 \\ Cl = & \underline{35{\cdot}5} \\ & 36{\cdot}5 \end{array}$$

The molecular weight of nitric acid is 63.

$$\begin{array}{lr} H & = 1 \\ N & = 14 \\ O_3 = 16 \times 3 & = \underline{48} \\ & 63 \end{array}$$

Sulphuretted hydrogen.

$$\begin{array}{lrl} H_2 = 1 \times 2 & = 2 & \\ S & = \underline{32} & \\ & 34 & \text{molecular weight.} \end{array}$$

Ammonia gas.

$$\begin{array}{lrl} N & = 14 & \\ H_3 = 1 \times 3 & = \underline{3} & \\ & 17 & \text{molecular weight.} \end{array}$$

Equivalent weight is the *weight* of an element or radicle which can replace or combine with *one part by weight* of hydrogen, and can be shortly expressed thus—

$$\text{Equivalent weight} = \frac{\text{Atomic weight.}}{\text{Active valency.}}$$

Thus, oxygen at weight 16, valency 2, equivalent weight $= \frac{16}{2} = 8$, or eight parts by weight of oxygen will combine with one part by weight of hydrogen, as in water H_2O. Again, if we place a bar of bright iron in a solution of copper sulphate, the iron will dissolve and the copper will be deposited in *equivalent* weights. The atomic weight of iron is 56, and in the ferrous state it is divalent. Atomic weight of copper is 63·5, and it is divalent. So equivalent weights will be $\frac{56}{2}$ and $\frac{63\cdot5}{2}$ or, in other words, 28 parts of iron will be dissolved in order to deposit 31·75 parts of copper.

Equivalent weights are important, because they are the weights of elements and radicles which are liberated when an electric current is passed through a series of solutions. Thus, if we send a current through four vessels, containing respectively: (1) acidulated water; (2) salt solution, NaCl; (3) copper sulphate solution, $CuSO_4$; (4) gold cyanide solution $Au(CN)_3$; if 1 gramme of hydrogen is liberated in the first vessel, we shall have in the second 23 grammes of sodium and 35·5 grammes of chlorine, in the third $\frac{63\cdot5}{2} = 31\cdot75$ grammes of copper, and in the fourth $\frac{197}{3} = 65\cdot7$ grammes of gold.

An element can only have one atomic weight, but it may have several equivalent weights, because its valency may vary. Thus, the equivalent weight of iron in the ferrous salts is $\frac{56}{2} = 28$; in the ferric salts, $\frac{56}{3} = 18\cdot6$.

USES OF TERMINATIONS.

In order to apply the correct names to the various chemical compounds, the student must become acquainted with the different terminations used in speaking of the various acids, salts, etc. For instance, he will continually have to use the terms *chloride*, *iodide*, ites = ous acid

sulphite, *sulphate*, and will often come across acids and salts, to the names of which the terminations *-ous* and *-ic* are affixed, such as *sulphurous*, *nitrous*, *sulphuric*, and *nitric* acids, *ferrous*, *ferric*, *mercurous* and *mercuric* salts. We will now proceed to explain the uses of the different terminations.

1. Sometimes an element, in uniting with hydrogen and oxygen to form an acid, unites with different quantities of oxygen to form different acids; the termination *-ic* is then applied to the acid containing the most oxygen, and the termination *-ous* to that containing the smaller proportion of oxygen; thus:

H_2SO_4 is sulphur*ic* acid.	H_2SO_3 is sulphur*ous* acid.
HNO_3 is nitr*ic* acid.	HNO_2 is nitr*ous* acid.
H_3AsO_4 is arsen*ic* acid.	H_3AsO_3 is arseni*ous* acid.
$HClO_3$ is chlor*ic* acid.	$HClO_2$ is chlor*ous* acid.

2. The termination *-ate* is applied to the salts of those acids that possess the termination *-ic*, and the termination *-ite* is applied to the salts of those acids that terminate in *-ous*; thus:

K_2SO_4 is sulph*ate*	of potassium.	K_2SO_3 is sulph*ite*	of potassium.
KNO_3 is nitr*ate*		KNO_2 is nitr*ite*	
K_3AsO_4 is arseni*ate*		K_3AsO_3 is arsen*ite*	
$KClO_3$ is chlor*ate*		$KClO_2$ is chlor*ite*	

3. Occasionally, after the naming of a group of acids, an acid has been discovered containing a greater proportion of oxygen than the one to which the termination *-ic* was applied; the prefix *per-* (abbreviation of *super, above*) is then attached to the name of the acid ending in *-ic*, to distinguish the new acid; thus:

$HClO_4$ is *perchloric* acid,
$HClO_3$ being *chloric* acid.

On the other hand, an acid is sometimes discovered

- ic
ous
hypo — ous

containing a smaller proportion of oxygen than the acid to which the termination *-ous* had been applied; the prefix *hypo-* (signifying *under*) is then attached to the name of the acid ending in *-ous*, to distinguish the new acid; thus: $HClO_4$ = perchloric acid
$HClO_3$ = chloric acid

$HClO_2$ being *chlorous* acid,
$HClO$ is *hypochlorous* acid.

3. When an acid contains an element for its acidulous radicle, the prefix *hydro-* (abbreviation of *hydrogen*) is used; thus:

HCl is *hydro*chloric acid.
HF is *hydro*fluoric acid.
HBr is *hydro*bromic acid.
HI is *hydr*iodic acid.

4. The termination *-ide* is used in connection with those compounds which contain *only two* elements or radicles.

$NaCl$ is chlor*ide* of sodium.
KI is iod*ide* of potassium.
FeS is sulph*ide* of iron.
HgO is ox*ide* of mercury.

As was mentioned in the article on the quantivalence of the elements, some elements are capable of exerting different combining powers; those compounds in which an element is exerting its full combining power are distinguished by having the termination *-ic* attached to their names, the termination *-ous* being attached to the names of those compounds in which the element is exerting part of its combining power only; thus:

$P^{v}_{2}O^{ii}_{5}$ is phosphor*ic*	anhydride.	$P^{iii}_{4}O^{ii}_{6}$ is phosphor*ous*	anhydride.
$As^{v}_{2}O^{ii}_{5}$ is arsen*ic*		$As^{iii}_{4}O^{ii}_{6}$ is arseni*ous*	
$Fe^{iii}Cl^{i}_{3}$ is ferr*ic* chloride.		$Fe^{ii}Cl^{i}_{2}$ is ferr*ous* chloride.	
$Sn^{iv}Cl^{i}_{4}$ is stann*ic* chloride.		$Sn^{ii}Cl^{i}_{2}$ is stann*ous* chloride.	

Sometimes the prefixes *per-*, and *proto-* or *sub-*, are respectively employed instead of the terminations *-ic* and *-ous*; thus, ferric chloride may be called *per*chloride of iron, and ferrous chloride the *proto*chloride or *sub*chloride of iron; stannic chloride may be called the *per*chloride of tin, and stannous chloride the *proto*chloride or *sub*chloride of tin.

CHAPTER V.

Chemical Equations — Classification of Chemical Equations — Methods of Writing Chemical Equations.

CHEMICAL EQUATIONS.

The changes that occur when two or more substances act chemically upon one another are represented by placing on the left the formulæ of the substances as they exist *before* the change, connected with each other by the sign $+$, signifying, as in algebra, addition; on the right are formulated the substances as they exist *after* the change, connected together, as before, by the sign $+$, and connected with the left-hand portion by the sign of equality $=$; such a collection of symbols is known as a **chemical equation.** A thorough knowledge of the representation of chemical reactions by means of equations is absolutely necessary, and careful attention should be given to this subject. An endeavour will be made now to simplify the matter by arranging it in a systematic and definite manner, commencing with reactions that are represented by simple equations, and then proceeding step by step to the representation of the more difficult and complex reactions.

A large number of chemical reactions come under one or more of the four following divisions, in each of which a typical equation constructed of letters represents the kind of action taking place:—

I. ANALYSIS (ἀνά, up; λύσις, separation):

$$AB = A + B.$$

II. SYNTHESIS (σύν, together; θέσις, placing):

$$A + B = AB.$$

III. SINGLE DECOMPOSITION:

$$AB + C = A + BC.$$

or

$$AB + C = AC + B.$$

IV. DOUBLE DECOMPOSITION:

$$AB + CD = AC + BD,$$

or

$$AB + CD = AD + BC.$$

We will now take several examples of equations that come under these four heads:—

I. ANALYSIS (typical equation $AB = A + B$).—Under this head will come those equations which represent the splitting up of a compound body into its elements, or into less complex bodies. Thus, when mercuric oxide is heated, it splits up into its elements mercury and oxygen:

$$HgO = Hg + O.$$

(*a*) This equation is not as yet quite correct, for it represents an atom of oxygen as possessing independent existence, which is an impossibility. We must, therefore, represent two molecules of mercuric oxide in the equation, which will then produce a molecule of free oxygen (O_2) which is capable of existing in the free state; thus:

$$2HgO = 2Hg + O_2.$$

cf. 44 In. Ch. K

The number is placed before the Hg to represent two molecules of mercury, for mercury is one of the three elements (Hg, Zn, Cd) that contain only one atom in the molecule.

The student must remember to represent the existence of molecules in equations, and therefore equations will frequently have to be doubled, as in the case of the one just given. In order to refer to a few more equations that come in the first division (Analysis), we will take the three following examples:—

(*b*) Oxide of silver when heated splits up into silver and oxygen:

$$2Ag_2O = 4Ag + O_2.$$

(*c*) The following equation represents the decomposition of water into its elements, a decomposition that can be brought about by means of electricity:—

$$2H_2O = 2H_2 + O_2.$$

In this equation two molecules of H_2O are taken, so that the liberation of a molecule of oxygen (O_2) may be represented.

(*d*) The next equation represents the manner in which chlorate of potassium ($KClO_3$) splits up, when heated, into chloride of potassium and oxygen:

$$2KClO_3 = 2KCl + 3O_2.$$

The equation $KClO_3 = KCL + 3O$ would not be correct since it represents the formation of a molecule and a half of oxygen, and half a molecule is incapable of a free existence. The large number 2 placed before the $KClO_3$ multiplies everything after it as far as the sign $=$; the small 3 placed under the O is therefore multiplied by the large 2.

II. SYNTHESIS (typical equation $A+B=AB$).—Equations of this kind represent the combination together of elements to form compounds, and also the combination of simple compounds to form more complex compounds.

(*a*) The following equation represents the formation of water by the union of hydrogen and oxygen :

$$2H_2 + O_2 = 2H_2O.$$

The equation $H_2 + O = H_2O$ would not be correct, as O represents an atom of oxygen which cannot exist in the free state (it will not be necessary to explain again why, in similar equations to this, the double number is taken to prevent the representation of a free atom).

(*b*) The next equation represents the formation of sulphide of iron (FeS) by the union of iron and sulphur (which can be effected by means of heat) :

$$2Fe + S_2 = 2FeS.$$

(*c*) The following equation represents the formation of sulphur dioxide (SO_2) by the combustion of sulphur in oxygen :

$$S_2 + 2O_2 = 2SO_2.$$

III. SINGLE DECOMPOSITION (typical equations $AB + C = A + BC$ and $AB + C = AC + B$).—The student will meet with numerous equations of this kind in the study of Chemistry. The following are a few examples :

(*a*) The action of zinc on hydrochloric acid (HCl), when chloride of zinc ($ZnCl_2$) is formed and hydrogen set free :

$$Zn + 2HCl = ZnCl_2 + H_2.$$

(*b*) The action of iron on dilute sulphuric acid (H_2SO_4), when sulphate of iron ($FeSO_4$) is formed and hydrogen set free :

$$2Fe + 2H_2SO_4 = 2FeSO_4 + 2H_2.$$

(*c*) The reduction of oxide of copper (CuO) to the metallic state by means of charcoal, a decomposition that is effected by heating the two together, when the carbon abstracts the oxygen, forming carbon dioxide (CO_2) :

$$2CuO + C = 2Cu + CO_2.$$

(*d*) The formation of reduced iron (finely-divided iron), which is obtained by passing hydrogen over heated ferric oxide (Fe_2O_3), when the hydrogen abstracts the oxygen, with the formation of water and free iron :

$$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O.$$

In this equation it is necessary to take $3H_2$ in order to furnish sufficient hydrogen to unite with the three atoms of oxygen contained in the Fe_2O_3.

IV. DOUBLE DECOMPOSITION (typical equations $AB + CD = AC + BD$ and $AB + CD = AD + BC$).—Equations of this class are the most general that the student will meet with, reactions of double decomposition being of most common occurrence. We will take several examples of such equations.

When an oxide of a metal dissolves in an acid, as a rule, double decomposition takes place, the metal of the oxide uniting with the acid radicle of the acid to form a salt, and the oxygen of the oxide uniting in its turn with the hydrogen of the acid to form water ; thus :

(*a*) Equation representing the action of hydrochloric acid (HCl) on oxide of zinc (ZnO):

$$ZnO + 2HCl = ZnCl_2 + H_2O.$$

(*b*) Equation representing the action of nitric acid (HNO_3) on oxide of copper (CuO):

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O.$$

(*c*) Equation representing the action of hydrochloric acid (HCl) on ferric oxide (Fe_2O_3):

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O.$$

When a hydrate of a metal dissolves in an acid double decomposition takes place, the metal of the hydrate uniting with the acid radicle of the acid to form a salt, and the radicle of the hydrate (HO) at the same time uniting with the hydrogen of the acid to form water; thus:

(*d*) Equation representing the action of hydrochloric acid on caustic potash (potassium hydrate or hydroxide):

$$KHO + HCl = KCl + H_2O.$$

(*e*) Equation representing the action of sulphuric acid on slaked lime (hydrate of calcium):

$$Ca(HO)_2 + H_2SO_4 = CaSO_4 + 2H_2O.$$

When solutions of two soluble salts are mixed together and an insoluble salt (called the precipitate) is produced, the reaction is generally one of double decomposition; thus:

(*f*) Equation representing the precipitation of sulphate of barium ($BaSO_4$) by adding sulphuric acid (H_2SO_4) to solution of chloride of barium ($BaCl_2$):

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

(*g*) Equation representing the precipitation of carbonate of calcium ($CaCO_3$) by the addition of solution of carbonate of sodium (Na_2CO_3) to solution of chloride of calcium ($CaCl_2$):

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl.$$

(*h*) Equation representing the precipitation of mercuric iodide (HgI_2) by the addition of solution of iodide of potassium (KI) to solution of mercuric chloride ($HgCl_2$):

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

Several equations are more complex than those that have been given as yet, the products of decomposition being frequently more numerous than two, and sometimes more than two substances taking part in a reaction. Nothing but actual practice can teach a student such reactions; but the writing of equations can be very much simplified by a classification, so far as that is practicable, which we will now give, together with some hints that may prove useful on the methods of writing equations.

(i) The number of atoms on the right-hand side of an equation must correspond with those on the left-hand side; this, indeed, is evident from the position of the sign of equality (=), for one side of an equation could not be equal to the other unless the number of atoms contained on the one side corresponded with those on the other. So that, after writing an equation, the student should always verify it, by seeing if the number of atoms are equal on each side.

(ii) Whenever a hydrate of a metal dissolves in an acid, a salt of the metal and water are produced.

EXAMPLES.

KHO Potassium hydrate.	$+$	HCl Hydrochloric acid.	$=$	KCl Potassium chloride.	$+$	H_2O Water.
$2KHO$ Potassium hydrate.	$+$	H_2SO_4 Sulphuric acid.	$=$	K_2SO_4 Potassium sulphate.	$+$	$2H_2O$ Water.
$Ca(HO)_2$ Calcium hydrate.	$+$	$2HCl$ Hydrochloric acid.	$=$	$CaCl_2$ Calcium chloride.	$+$	$2H_2O$ Water.
$Zn(HO)_2$ Zinc hydrate.	$+$	H_2SO_4 Sulphuric acid.	$=$	$ZnSO_4$ Zinc sulphate.	$+$	$2H_2O$ Water.
$2Fe(HO)_3$ Ferric hydrate.	$+$	$6HCl$ Hydrochloric acid.	$=$	$2FeCl_3$ Ferric chloride.	$+$	$6H_2O$ Water.
$Cu(HO)_2$ Copper hydrate.	$+$	$2HNO_3$ Nitric acid.	$=$	$Cu(NO_3)_2$ Cupric nitrate.	$+$	$2H_2O$ Water.

When commencing to write an equation of this class, the formulæ of the hydrate, acid, and salt formed should first be written down, the formula of the salt will then usually indicate the number of molecules of hydrate and acid required.

(iii) When an oxide of a metal dissolves in an acid, as a rule, a salt of the metal and water are produced, *the only exceptions being the peroxides or higher oxides of the metals.*

Q. $BaO_2 + 2HCl = BaCl_2 + H_2O_2$

EXAMPLES.

$$\underset{\text{Barium oxide.}}{\mathrm{BaO}} + \underset{\text{Hydrochloric acid.}}{\mathrm{2HCl}} = \underset{\text{Barium chloride.}}{\mathrm{BaCl_2}} + \underset{\text{Water.}}{\mathrm{H_2O}}$$

$$\underset{\text{Calcium oxide.}}{\mathrm{CaO}} + \underset{\text{Hydrochloric acid.}}{\mathrm{2HCl}} = \underset{\text{Calcium chloride.}}{\mathrm{CaCl_2}} + \underset{\text{Water.}}{\mathrm{H_2O}}$$

$$\underset{\text{Magnesium oxide.}}{\mathrm{MgO}} + \underset{\text{Sulphuric acid.}}{\mathrm{H_2SO_4}} = \underset{\text{Magnesium sulphate.}}{\mathrm{MgSO_4}} + \underset{\text{Water.}}{\mathrm{H_2O}}$$

$$\underset{\text{Ferric oxide.}}{\mathrm{Fe_2O_3}} + \underset{\text{Hydrochloric acid.}}{\mathrm{6HCl}} = \underset{\text{Ferric chloride.}}{\mathrm{2FeCl_3}} + \underset{\text{Water.}}{\mathrm{3H_2O}}$$

$$\underset{\text{Antimony oxide.}}{\mathrm{Sb_2O_3}} + \underset{\text{Hydrochloric acid.}}{\mathrm{6HCl}} = \underset{\text{Antimony chloride.}}{\mathrm{2SbCl_3}} + \underset{\text{Water.}}{\mathrm{3H_2O}}$$

$$\underset{\text{Lead oxide.}}{\mathrm{PbO}} + \underset{\text{Nitric acid.}}{\mathrm{2HNO_3}} = \underset{\text{Lead nitrate.}}{\mathrm{Pb(NO_3)_2}} + \underset{\text{Water.}}{\mathrm{H_2O}}$$

$$\underset{\text{Copper oxide.}}{\mathrm{CuO}} + \underset{\text{Nitric acid.}}{\mathrm{2HNO_3}} = \underset{\text{Copper nitrate.}}{\mathrm{Cu(NO_3)_2}} + \underset{\text{Water.}}{\mathrm{H_2O}}$$

As indicated on the previous page, it is best to write down the formulæ of the oxide and the acid employed on the left-hand side of the equation, and the formula of the salt produced on the right. It will then be obvious how many molecules of the acid should be taken: thus, in the last equation of the above group, the formula $Cu(NO_3)_2$ indicates that $2HNO_3$ must be taken to furnish the $(NO_3)_2$, the 2H of the acid and the O of the oxide will then be in the proportion to form water.

(iv) Whenever a carbonate of a metal dissolves in an acid, a salt of the metal, water, and carbon dioxide (carbonic acid gas) are produced, the latter being evolved with effervescence.

EXAMPLES.

K_2CO_3	+	$2HCl$	=	$2KCl$	+	CO_2	+	H_2O
Potassium carbonate.		Hydrochloric acid.		Potassium chloride.		Carbon dioxide.		Water.

Na_2CO_3	+	H_2SO_4	=	Na_2SO_4	+	CO_2	+	H_2O
Sodium carbonate.		Sulphuric acid.		Sodium sulphate.		Carbon dioxide.		Water.

$CaCO_3$	+	$2HNO_3$	=	$Ca(NO_3)_2$	+	CO_2	+	H_2O
Calcium carbonate.		Nitric acid.		Calcium nitrate.		Carbon dioxide.		Water.

In these equations the radicle of the carbonate CO_3 splits up into CO_2 and O, the former escaping and the latter uniting with the H_2 of the acid to form water.

(v) When a metal dissolves in *hydrochloric acid*, a chloride of the metal is always formed, and hydrogen evolved.

EXAMPLES.

Zn	+	$2HCl$	=	$ZnCl_2$	+	H_2
Zinc.		Hydrochloric acid.		Zinc. chloride.		Hydrogen.

$2Fe$	+	$4HCl$	=	$2FeCl_2$	+	$2H_2$
Iron.		Hydrochloric acid.		Ferrous chloride.		Hydrogen.

(vi) When a metal dissolves in *dilute sulphuric acid*, a sulphate of the metal is always formed and hydrogen evolved.

EXAMPLES.

Zn	+	H_2SO_4	=	$ZnSO_4$	+	H_2
Zinc.		Sulphuric acid.		Zinc sulphate.		Hydrogen.

Zn + H_2SO_4 =

2Fe	+	$2H_2SO_4$	=	$2FeSO_4$	+	$2H_2$
Iron.		Sulphuric acid.		Ferrous sulphate.		Hydrogen.

(vii) When a metal dissolves in *strong sulphuric acid*, a sulphate of the metal is formed and sulphur dioxide (SO_2) evolved; the only common metals whose sulphates are made by the action of strong sulphuric acid on them are copper, mercury, and silver. ?

EXAMPLES.

2Cu	+	$4H_2SO_4$	=	$2CuSO_4$	+	$2SO_2$	+	$4H_2O$
Copper.		Sulphuric acid.		Copper sulphate.		Sulphur dioxide.		Water.
Hg	+	$2H_2SO_4$	=	$HgSO_4$	+	SO_2	+	$2H_2O$
Mercury.		Sulphuric acid.		Mercuric sulphate.		Sulphur dioxide.		Water.
2Ag	+	$2H_2SO_4$	=	Ag_2SO_4	+	SO_2	+	$2H_2O$
Silver.		Sulphuric acid.		Silver sulphate.		Sulphur dioxide.		Water.

It will be noticed that *twice as much acid* is aken as is required to furnish SO_4 for the sulphate, he extra SO_4 splitting up into SO_2 and O_2, the ormer escaping and the latter uniting with the hydrogen of the acid to form water.

(viii) The ordinary metals (with the exception of tin, antimony, arsenic, and zinc), when acted upon with slightly diluted nitric acid, form metallic nitrates and evolve nitrogen dioxide (NO).

tin gives NO_2
Zn - NH_4

EXAMPLES.

6Ag	+	$8HNO_3$	=	$6AgNO_3$	+	2NO	+	$4H_2O$
Silver.		Nitric acid.		Silver nitrate.		Nitrogen dioxide.		Water.
3Cu	+	$8HNO_3$	=	$3Cu(NO_3)_2$	+	2NO	+	$4H_2O$
Copper.		Nitric acid.		Copper nitrate.		Nitrogen dioxide.		Water.

$3Pb$	$+ 8HNO_3 =$	$3Pb(NO_3)_2 +$	$2NO$	$+ 4H_2O$
Lead.	Nitric acid.	Lead nitrate.	Nitrogen dioxide	Water.
$3Hg$	$+ 8HNO_3 =$	$3Hg(NO_3)_2 +$	$2NO$	$+ 4H_2O$
Mercury.	Nitric acid	Mercuric nitrate.	Nitrogen dioxide.	Water.
$2Bi$	$+ 8HNO_3 =$	$2Bi(NO_3)_3 +$	$2NO$	$+ 4H_2O$
Bismuth.	Nitric acid.	Bismuth nitrate.	Nitrogen dioxide.	Water.

In all these equations *eight molecules of nitric acid* ($8HNO_3$) are taken; a sufficient number of atoms of the metal are then worked into the equation to unite with *six* out of the eight equivalents of the nitric radicle present in the eight molecules of nitric acid, the remaining two equivalents of the nitric radicle ($2NO_3$) then split up into $2NO$ and $4O$, the former escaping and the latter uniting with the hydrogen of the nitric acid to form water.

Part II.

THE NON-METALLIC ELEMENTS AND THEIR PRINCIPAL COMPOUNDS.

solation and ~~Character~~ of Hydrogen ?

CHAPTER I.

HYDROGEN.

Hydrogen—Modes of Preparation—Preparation of Hydrogen from Water—Properties of Hydrogen—Combustion—Graham's Law of Diffusion—Test for Hydrogen.

H_2^I 1

HYDROGEN.

Symbol, H ; *molecule*, H_2 ; *monad; atomic weight*, 1 ; *molecular weight*, 2 ; *liquefies at* —253°.

HYDROGEN exists in nature principally in combination with oxygen in the form of water, and it owes the derivation of its name (from ὕδωρ, water; γεννάω, I produce) to the fact that when united with oxygen in certain proportions, it produces water.

I **Modes of preparation.**—(i) Hydrogen is
most conveniently prepared by the action of diluted
30% sulphuric acid on the metal zinc. Pieces of granu-
lated zinc are placed in a generating flask, to which 1
is adapted a cork provided with a bent delivery-tube 2
and a long funnel; sufficient water is then poured 3
into the flask to cover the zinc, and on pouring strong
sulphuric acid down the funnel, hydrogen is evolved 4
with brisk effervescence, and may be collected over
water (Fig. 1), after sufficient time has been allowed to
elapse for the escape of the air contained in the flask.

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + \underset{\text{Hydrogen.}}{H_2}$$

Hydrogen so obtained is never pure, it may contain (1) hydrogen arsenide from the arsenic in the zinc; (2) oxides of nitrogen from the nitric acid in the sulphuric acid; (3) sulphur dioxide and hydrogen sulphide if the sulphuric acid becomes heated during the reaction, because the nascent hydrogen then reduces the sulphuric acid; (4) water vapour.

H_2SO_4

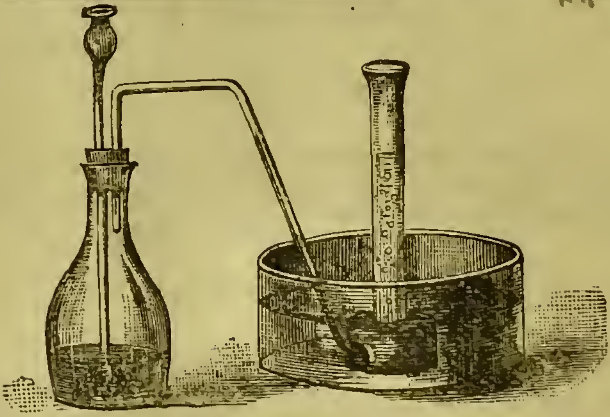


Fig 1.—Preparation of Hydrogen from Zinc and Sulphuric Acid.

These impurities can be removed by passing the gas through four U-tubes: the first is filled with broken glass moistened with lead nitrate solution, this removes the H_2S; the second with silver sulphate, which removes the AsH_3; the third contains caustic potash, which removes the SO_2 and oxides of nitrogen; the fourth with strong sulphuric acid, which removes the water.

(ii) In a similar manner hydrogen may be prepared by the action of diluted sulphuric acid on the metal iron.

$$\underset{\text{Iron.}}{2Fe} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Ferrous sulphate}}{2FeSO_4} + \underset{\text{Hydrogen.}}{2H_2}$$

(iii) By the action of hydrochloric acid on the

Zn Ca K Na – [illegible] molecule

metal zinc or on the metal iron, hydrogen is also evolved.

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Zinc chloride.}}{ZnCl_2} + \underset{\text{Hydrogen.}}{H_2}$$

$$\underset{\text{Iron.}}{2Fe} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Ferrous chloride.}}{2FeCl_2} + \underset{\text{Hydrogen.}}{2H_2}$$

(iv) Hydrogen may be obtained from water (*a*) by the *electrolysis* of water (see *water*, page 74), (*b*) by abstracting the oxygen from water, by passing steam over red-hot iron turnings contained in a heated iron pipe; the iron unites with the oxygen of the steam to form the black magnetic oxide of iron (Fe_3O_4), and free hydrogen passes on. This constitutes Barff's process for coating articles made of iron with a thin coating of the magnetic oxide of iron, which forms an extremely hard surface, and effectually prevents any future rusting of the article.

$$\underset{\text{Iron.}}{3Fe} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Magnetic oxide of iron.}}{Fe_3O_4} + \underset{\text{Hydrogen.}}{4H_2}$$

[illegible] e.g. Steam passed over red hot coke. Compounds of C & H are also formed

(*c*) By the action of either of the metals potassium or sodium on water at ordinary temperatures. Both these metals are lighter than water, and if either of them be thrown upon water, a violent action takes place, hydrogen being evolved. If the hydrogen is to be collected, it is necessary to catch the piece of potassium or sodium in some wire gauze, which is then held beneath the water under an inverted jar full of water, within which the hydrogen will then collect (Fig. 2).

K Na Ca Ba Sr

These metals liberate one-half of the hydrogen of the water, uniting with the other half and with the

Fr water & by cert. metals

water rendering it soapy to touch & [illegible]
alkaline to litmus

oxygen to form respectively the hydrate or hydroxide of the metal, thus :

$$\underset{\text{Potassium.}}{2K} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Potassium. hydrate.}}{2KHO} + \underset{\text{Hydrogen.}}{H_2}$$

$$\underset{\text{Sodium.}}{2Na} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Sodium hydrate.}}{2NaHO} + \underset{\text{Hydrogen.}}{H_2}$$

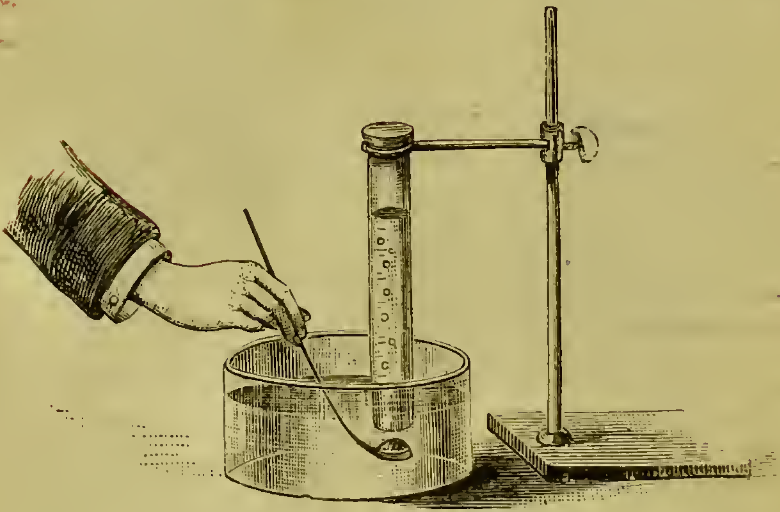


Fig. 2.—Preparation of Hydrogen from Potassium and Water.

Properties.—Hydrogen is a colourless, tasteless, and odourless gas. It was liquefied first by Olszewski ; recently Dewar has obtained it in larger quantity : he states that its specific gravity is 0·07, it is therefore by far the lightest liquid known ; it is transparent and colourless, and boils at —253°, about 20° above the absolute zero (—273°), it solidifies at —257° to an ice-like solid. It is the lightest body known, and its specific gravity is represented as 1, the specific gravities of other gases representing the number of times they are heavier than hydrogen ; air is 14·4 times heavier than hydrogen. The weight of a litre of hydrogen, taken at 0° C. and 760 mm. barometric pressure, is ·0896 gramme, and is known as the *crith* (from κριθή, a barleycorn); 2 grammes of hydrogen at 0° C. and 760 mm. barometric pressure occupy 22·4 litres (this latter fact will be found extremely useful in converting weights of various gases into volumes). Hydrogen is combustible, burning with an almost invisible flame if pure, and forming, by union with the oxygen of the air, water; it is a non-supporter of combustion.

By the term combustion, as ordinarily employed, is meant union with the oxygen of the air, such union being accompanied by the production of heat and light, so that combustion may be defined as oxidation in which the chemical action is sufficiently great to be accompanied by the evident production of heat and light. It must, however, be clearly understood that the terms *combustible* and *supporter of combustion* are purely relative; thus, hydrogen is combustible in oxygen, and oxygen is a supporter of combustion; but if the atmosphere consisted of hydrogen, then oxygen would burn in it, and would be the combustible body, the hydrogen then being the supporter of combustion. It therefore follows, according to the accepted meanings of these terms, that a combustible body cannot be also a supporter of combustion, nor, conversely, can a supporter of combustion be combustible.

The formation of water by the combustion of hydrogen can be demonstrated by allowing the jet of hydrogen to burn within a cool bell-jar, when the water condenses on the sides of the glass (Fig. 3).

The hydrogen flame is accompanied with the generation of intense heat, of which advantage is taken in the production of the lime-light. A jet of burning hydrogen (produced by the combustion of hydrogen with pure oxygen) is directed on to a piece of lime, the particles of which are raised to such a high temperature that they become incandescent, and glowing at a white heat emit the dazzling light known as the lime-light. The reason why the ordinary hydrogen flame emits no light is, that there is present in it no solid matter that can be raised to a white heat and so emit light, for it is essential, for a flame to emit light, that there should be present in the flame some solid matter or dense vapour capable of being rendered incandescent; in the case of the lime-light, the lime is the solid matter that is introduced into the flame, and is rendered incandescent by the intense heat generated by the burning hydrogen.

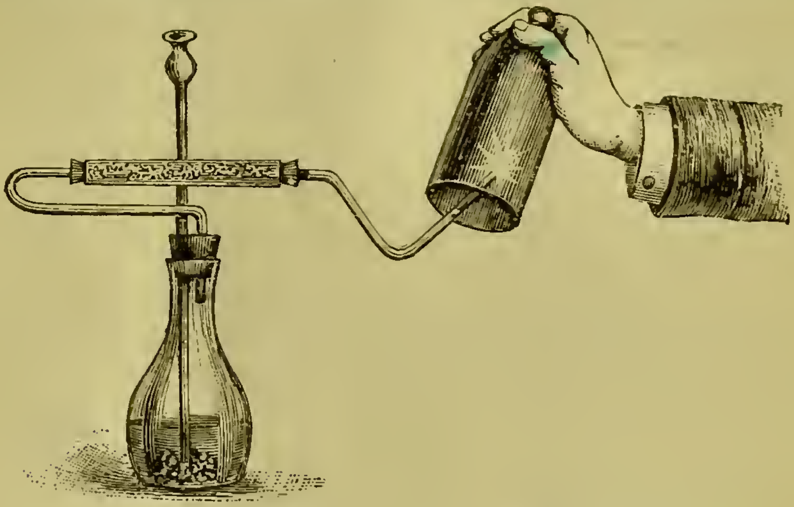


Fig. 3.—Formation of Water by the Combustion of Hydrogen.

When a light is applied to a mixture of hydrogen and oxygen, the union of the two gases is accompanied by an explosion; two volumes of hydrogen unite with one volume of oxygen, or two parts by weight of hydrogen with sixteen of oxygen, to form water.

Hydrogen is not appreciably soluble in water; it is not, in the ordinary sense of the term, a poisonous gas, although it is incapable of supporting life. It is the most diffusible of all the gases; by *diffusion* is meant the property that all gases have of mixing with one another, even in opposition to the force of gravitation; thus, if two flasks are taken (Fig. 4), the lower one filled with oxygen and the upper one with hydrogen, and are connected by a long piece of narrow glass tubing passing through a perforated cork in each flask, although the heavier gas, oxygen, is at the bottom, and the lighter, hydrogen, at the top, yet the hydrogen will tend to diffuse downwards into the oxygen, and the oxygen will tend to diffuse upwards

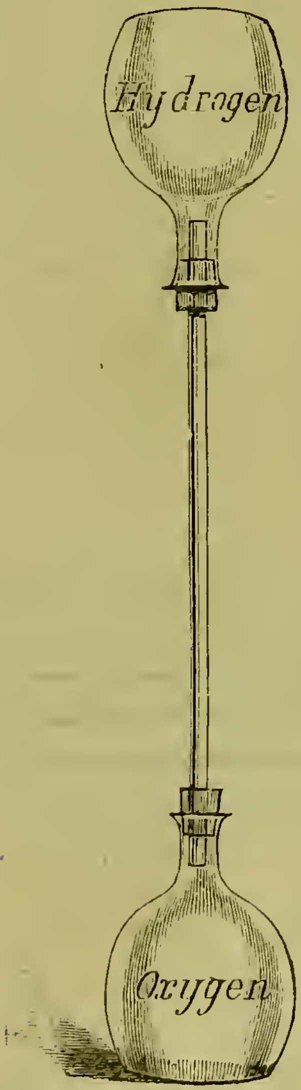


Fig. 4.—Apparatus for Diffusion of Gases.

into the hydrogen, until the two gases are completely mixed. It is by this property of diffusion that a small quantity of a bad-smelling gas escaping, say into the corner of a room, soon demonstrates by its odour that it has become mixed with the entire atmosphere of the room.

All gases do not diffuse at the same rate, lighter gases diffuse more quickly than heavier ones; the relation existing between the rate of diffusion of a gas and its specific gravity is formulated in what is known as **Graham's law of the diffusion of gases,** which is, *that gases diffuse inversely as the square roots of their specific gravities.* For instance, the specific gravity of hydrogen is 1, that of oxygen 16; the square root of the former is 1, of the latter 4; these numbers inverted give the rate of diffusion of hydrogen as four times that of oxygen.

Hydrogen is a reducing agent, by which is meant that, under certain conditions, it is capable of abstracting oxygen from many bodies containing that element; for instance, if hydrogen be passed over fragments of red-hot copper oxide, the oxygen is abstracted by the hydrogen to form water, the copper oxide being *reduced* to the metallic state; thus:

$$\underset{\text{Copper oxide.}}{2CuO} + \underset{\text{Hydrogen.}}{2H_2} = \underset{\text{Copper.}}{2Cu} + \underset{\text{Water.}}{2H_2O}$$

Test.—The best test for hydrogen is that it burns with an almost invisible flame, forming nothing but water. It is also the lightest of all the ordinary gases. In some respects hydrogen resembles the metals, thus it is liberated, like the metals, at the negative electrode. It is also absorbed by several metals, notably by palladium and potassium, forming metallic-looking alloys having the formulæ Pd_2H and K_2H. Liquid hydrogen, however, is quite unlike a metallic substance.

Methods of prep.
2. $KClO_3$
3. MnO_2
4. $K_2Cr_2O_7$
5. Chlorine [illegible]
6. fr. air. Baryta Process.
7. Mixture of [illegible] by catalys

Heat. $MnO_2 + H_2SO_4$.

Isolation and Character

CHAPTER II. Oxygen

OXYGEN—OZONE.

Oxygen—Modes of Preparation—Preparation of Oxygen from Water—Electrolysis of Water—Preparation of Oxygen from Air—Properties of Oxygen—Test for Oxygen—Oxygen in Relation to Respiration—Ozone—Preparation—Tests for Ozone.

OXYGEN.

Most Electro-negative Element

Symbol, O; *molecule*, O_2; *dyad*; *atomic weight*, 16; *molecular weight*, 32; *liquefies at* —183°.

OXYGEN is present to a very large extent in nature. In the compounds composing the solid crust of the earth it exists in considerable proportions, principally in chalk and limestone (calcium carbonate—$CaCO_3$), sand and flint (silica—SiO_2), and clay (aluminium silicate—$Al_2Si_2O_7 + 2H_2O$). It constitutes $\frac{8}{9}$ by weight of water, and about $\frac{2}{9}$ by weight of air. Its name is derived from ὀξύς, acid, and γεννάω, I produce, since at one time it was believed that it entered into the composition of all acids, a belief which for a long time has been known to be erroneous.

Modes of preparation.—(1) By heating mercuric oxide (red oxide of mercury):

$$\underset{\text{Mercuric oxide.}}{2HgO} = \underset{\text{Mercury.}}{2Hg} + \underset{\text{Oxygen.}}{O_2}$$

This method, although by no means the best one for obtaining oxygen, is of interest from the fact that it was in this way that oxygen was first obtained and discovered by Priestley in 1774; mercury possesses the property, when heated to a temperature of 320°

on highly oxidised Salts.

nitre (KNO3)

with exposure to air, of slowly absorbing oxygen from the air, and forming mercuric oxide, which, when the temperature is raised a little higher, evolves its oxygen, the metal mercury being left. In 1775 it was obtained independently by Scheele, by heating strong sulphuric acid with black oxide of manganese:

$2MnO_2$	+	$2H_2SO_4$	=	$2MnSO_4$	+	$2H_2O$	+	O_2
Manganese black oxide.		Sulphuric acid		Manganese sulphate.		Water.		Oxygen.

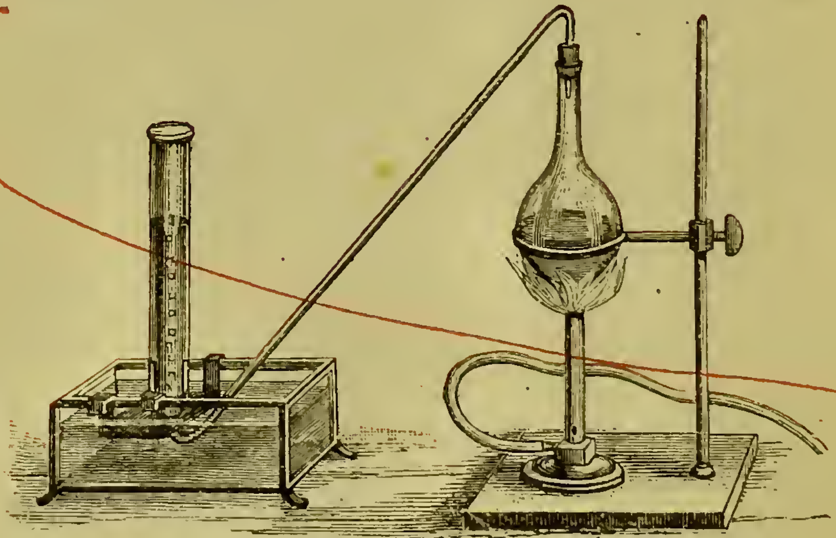


Fig. 5.—Preparation of Oxygen.

(ii) One of the best ways of obtaining oxygen, for experimental purposes, is by heating chlorate of potassium in a glass flask, to which is fitted a perforated cork and bent tube for conveying the gas to a pneumatic trough, where it can be collected over water (Fig. 5).

The whole of the oxygen of the chlorate of potassium is evolved, chloride of potassium being left:

$2KClO_3$	=	$2KCl$	+	$3O_2$
Potassium chlorate.		Potassium chloride.		Oxygen.

(iii) Oxygen can be obtained from potassium the action of strong acid. Cf. $KMnO_4$ + Peroxides heated with H_2SO_4 also evolve O.

chlorate at a much lower temperature by mixing it with one-fifth of its weight of manganese dioxide. The chlorate when heated alone begins to evolve oxygen about 370°; but the mixture gives off its oxygen at 250°. The manganese dioxide is found unaltered at the end of the reaction, and can be used again with a fresh quantity of potassium chlorate. When a substance affects a decomposition in this way without itself being apparently altered in composition, it is said to act by *catalysis.*

(iv) Oxygen may be obtained by strongly heating manganese dioxide (black oxide of manganese) in a gun-barrel closed at one end, and fitted at the other end with a perforated cork and tubing for carrying off the gas. The manganese dioxide only loses one-third of its oxygen, a lower oxide of manganese being left:

$$\underset{\text{Manganese dioxide.}}{3MnO_2} = \underset{\text{Trimanganic tetroxide.}}{Mn_3O_4} + \underset{\text{Oxygen.}}{O_2}$$

(v) Oxygen may be obtained by heating powdered bichromate of potassium with strong sulphuric acid.

$$\underset{\text{Potassium bichromate.}}{2K_2Cr_2O_7} + \underset{\text{Sulphuric acid.}}{8H_2SO_4} = \underset{\text{Chromium sulphate.}}{2Cr_2(SO_4)_3} + \underset{\text{Potassium sulphate.}}{2K_2SO_4} + \underset{\text{Water.}}{8H_2O} + \underset{\text{Oxygen.}}{3O_2}$$

Water:

(vi) Oxygen may be obtained from water by two processes: (*a*) the electrolysis of water, and (*b*) decomposition of it by means of chlorine.

(*a*) *Electrolysis of water.*—This consists in decomposing water into its elements by means of a current of electricity. A glass vessel, A (Fig. 6), is taken, into which project two platinum electrodes, which are connected through the bottom of the vessel with the wires B and C, which in their turn are connected respectively with the positive and negative poles of a battery. Some water acidulated with sulphuric acid (to render it a better conductor of electricity) is placed in A, and two glass tubes, D and E, are filled with this acidulated water, and then inverted over the platinum electrodes. On passing the current of electricity, the water is decomposed into its elements, the hydrogen being set free at the negative pole or electrode (C), and the oxygen at the positive pole or electrode (B), the hydrogen collecting in the tube placed over the negative electrode, and the oxygen in the tube over the positive electrode. The volume of hydrogen evolved is double that of the oxygen, although if the volumes of the gases are very accurately compared, it will be found that the oxygen measures slightly less than one-half the volume of the hydrogen, this slight difference being due to the greater solubility of oxygen in water, as compared with hydrogen.

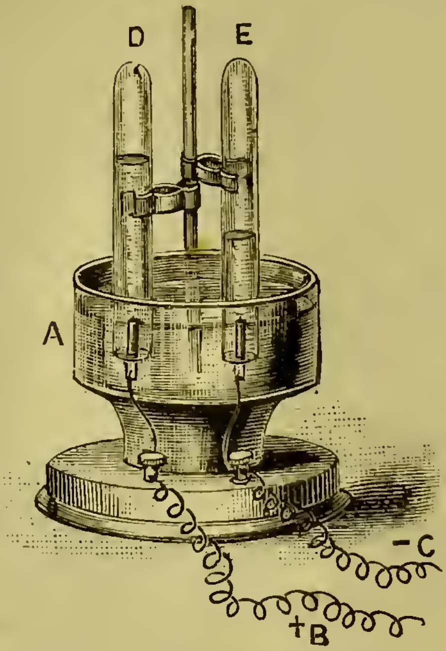


Fig. 6.—Electrolysis of Water.

(*b*) *Decomposition of water by chlorine.*—If chlorine and steam be passed through a porcelain tube containing fragments of pumice-stone heated to bright redness, the chlorine unites with the hydrogen of the water, forming hydrochloric acid, and the oxygen is set free:

$$\underset{\text{Chlorine.}}{2Cl_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Hydrochloric acid.}}{4HCl} + \underset{\text{Oxygen.}}{O_2}$$

If the mixture of hydrochloric acid gas and oxygen be passed through a strong solution of caustic potash, the former is absorbed, potassium chloride being formed, and the oxygen is then obtained in the pure state.

From air

fr. air

(vii) Oxygen may be obtained from the atmosphere, in which it naturally occurs mixed with nitrogen in the proportions of 21 volumes of oxygen to 79 of nitrogen. As there is no method of absorbing the nitrogen from a limited amount of air, and so leaving the oxygen in the pure state, the method that must be resorted to, if it is desired to obtain pure oxygen from the air, is to heat some substance in contact with the air, which at one temperature will absorb or combine with the oxygen of the air, and at another temperature will give up in a pure state the oxygen so taken from the air. The simplest process for effecting this is the baryta process.

The baryta process.—This process depends upon the metal barium possessing two oxides, a lower one, baryta (BaO), and a higher one, barium dioxide (BaO_2). If baryta (BaO) be raised to a dull red heat, and air be passed over it, the oxygen of the air is absorbed, converting the baryta into barium dioxide (BaO_2): ?

$$\underset{\text{Baryta.}}{2BaO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Barium dioxide}}{2BaO_2}$$

Heating Barium peroxide

$4CrO_3 = 2Cr_2O_3 + 3O_2$.
$2BaO_2 = 2BaO + O_2$
$2Ag_2O = 4Ag + O_2$
$2PtO_2 = 2Pt + 2O_2$

If now the barium dioxide be raised to a bright red heat, it is resolved into baryta and oxygen, and so the oxygen absorbed from the air is obtained in a pure state :

$$\underset{\text{Barium dioxide.}}{2BaO_2} = \underset{\text{Baryta.}}{2BaO} + \underset{\text{Oxygen..}}{O_2}$$

Instead of decomposing the barium peroxide by raising the temperature, it has been found more advantageous to bring about the reaction by reducing the pressure in the tube or furnace containing the heated dioxide. Care is also taken to purify the air from carbon dioxide, etc., before passing it over the baryta ; thus modified the process is now employed on a manufacturing scale for obtaining pure oxygen.

Properties.—The specific gravity of oxygen is 16 ; it is a little heavier than air. It is colourless, tasteless, and odourless. Although non-combustible, it is a powerful supporter of combustion, substances burning in oxygen much more brilliantly than they do in air. For instance, phosphorus burns with a most intense light in oxygen, and even a steel-wire spiral tipped with a piece of burning tinder and placed in a jar of oxygen will burn brilliantly, producing a shower of sparks (Fig. 7).

At —183° oxygen is converted into a pale blue liquid which is attracted by a powerful magnet.

Oxygen is soluble in water, 100 volumes of water dissolving about 3 volumes of oxygen, and it is by means of this dissolved oxygen that fishes' blood, circulating through the gills, becomes aërated. Oxygen is, of course, non-poisonous, being the life-sustaining principle of the air ; but if an animal be kept in pure oxygen it rapidly emaciates, on account of the increased waste of tissue substance generated by the absorption of pure oxygen into the blood, and this occurs although the animal may be plentifully supplied with food, which it greedily devours.

2

Test.—The best test for pure oxygen is one depending upon its remarkable power of supporting combustion; if a piece of wood which has been made incandescent or glowing at one extremity, be plunged into a jar of oxygen, it bursts into flame. A more delicate test is to add a little nitric oxide; this is a colourless gas which turns deep red when it comes into contact with free oxygen, being converted into nitric peroxide.

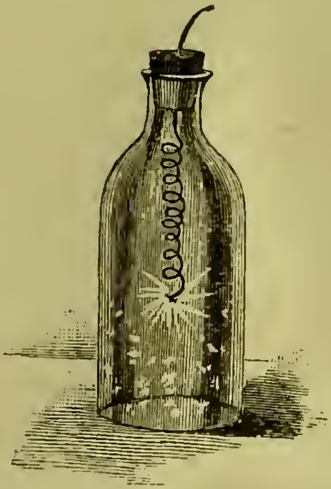


Fig. 7.—Combustion of Steel-wire in Oxygen.

NO

Oxygen in relation to respiration.—The oxygen of the air taken into the lungs, during inspiration, dissolves in part in the moisture covering the walls of the pulmonary air-cells, and so passes, by a process of osmosis, through the walls of the blood-capillaries into the blood, where it unites with the hæmoglobin or colouring matter of the blood, to form a compound called oxyhæmoglobin. In this compound the oxygen is conveyed by the blood to all the tissues of the body, which abstract the oxygen from its loose union with the hæmoglobin, and undergo by means of it a process of combustion, and the heat resulting from these chemical changes suffices to maintain the temperature of the human body. One of the necessary and chief products of the oxidation of the animal tissues is carbon dioxide, which passes away in the expired air. There is thus a constant interchange of oxygen from the atmosphere, and of carbon dioxide from the blood, the air taken into the lungs losing four per cent. of oxygen and gaining in its place four per cent. of carbon dioxide. This carbon dioxide, which passes out in the expired air into the atmosphere, does not accumulate there, but is absorbed by the leaves of plants (through small openings called *stomata*) and brought into contact with the chlorophyll or green colouring-matter of the leaves; this during the day decomposes the carbon dioxide: the oxygen is returned to the air, and so the normal composition of the atmosphere is maintained; at the same time the chlorophyll possesses the power of causing the carbon of the carbon dioxide to unite with the elements of water, and thus become converted into sugar, starch, and other organic substances.

Oxygen combines with every element, excepting fluorine, to form oxides. (+ Bromine ?)

These oxides may be divided into three classes.

1. Oxides which form acids, as sulphur trioxide, phosphorus pentoxide, etc.

2. Oxides which form bases, as potassium oxide, calcium oxide, etc.

3. Neutral oxides, such as black oxide of manganese.

OZONE.

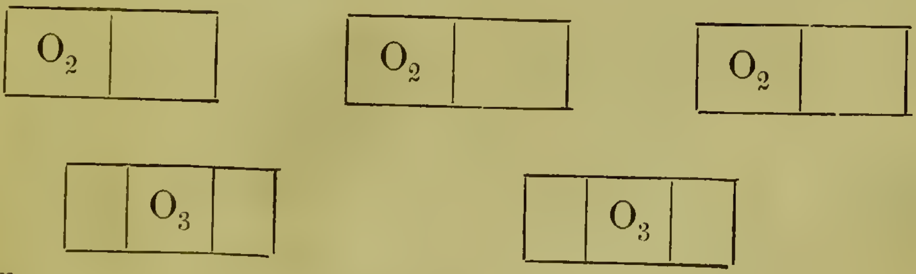
Formula, O_3; *molecular weight*, 48.

Ozone (from ὄζω, I smell) is an allotropic form of oxygen, three volumes being condensed into two. It occurs naturally in the atmosphere in very small quantities, being produced from the oxygen of the air either by electrical currents generated during a (!)

thunderstorm, or by the weak currents of frictional electricity generated by the friction of large masses of water (such as the sea) against the air, or possibly by the evaporation of water and aromatic bodies (such as turpentine) in presence of sunlight. ② ③

Two **Modes of preparation.**—Ozone is prepared by effecting the condensation of three volumes of oxygen into two, but by whatever process this may be effected, it is impossible to convert all the oxygen into ozone; in other words, ozone cannot be obtained in a pure state, but always contains admixed oxygen, a mixture containing about 20 per cent. of ozone to 80 per cent. of oxygen being about the strongest that has ever been made. This condensation of oxygen into ozone may be effected in the following ways.

(i) By the silent passage of electricity through damp oxygen or air; the peculiar odour noticed when a frictional electrical machine is being worked is due to the production of ozone by this process. The change may be represented as follows, where the production of two ozone molecules from three oxygen molecules is depicted:—



or,

$$\underset{\text{Oxygen.}}{3O_2} = \underset{\text{Ozone.}}{2O_3}.$$

(ii) Ozone may be prepared by exposing a stick of phosphorus to moist and warm oxygen or air. This is best effected by placing a stick of phosphorus at the bottom of a bottle containing sufficient water to cover partially the phosphorus, loosely plugging the mouth of the bottle, and placing it for half an hour near a fire. At the end of that time ozone will be found in the air of the bottle, if the proper tests are applied.

Properties.—The specific gravity of ozone is 24, and it is heavier than air; it is colourless, but possesses a peculiar odour which has been compared to that of diluted chlorine, or to phosphorus slowly oxidising. It is non-combustible, but is a supporter of combustion, and is slightly soluble in water. It is a powerful bleaching and oxidising agent, being capable of oxidising such metals as mercury and silver in the cold. It rapidly destroys cork, india-rubber, and other organic substances. It is an irritant to the eyes, nose, and bronchial tract, when present in the air in moderate quantities. It is completely decomposed when heated to 300°, and is absorbed by turpentine.

Tests.—The ordinary method for detecting ozone in the air depends upon the power that ozone possesses of liberating iodine from iodide of potassium, the presence of free iodine being shown by the blue colour that it gives with a solution of starch. A piece of filter paper is moistened with a mixed solution of iodide of potassium and starch, and is then suspended for some time in a current of the air to be tested, when, if ozone be present, it will assume a blue colour. The objections to the validity of this test are that other bodies besides ozone may be present in the air, which also possess the property of liberating iodine from iodide of potassium, and so giving a blue colour to the starch; these bodies are chlorine and nitrogen ~~tetrox~~ide. It will be seen from the following equations that when ozone liberates the iodine from iodide of potassium it first forms potassium oxide, which, with water, forms caustic potash, a body that is alkaline to test-paper; whereas chlorine and nitrogen tetroxide in liberating iodine from iodide of potassium form respectively chloride of potassium and nitrite of potassium, both of which are neutral to test-paper.

$6KI$	+	O_3	=	$3K_2O$	+	$3I_2$
Potassium iodide.		Ozone.		Potassium oxide.		Iodine

then

$3K_2O$	+	$3H_2O$	=	$6KHO$		
Potassium oxide.		Water.		Caustic potash (Potassium hydrate).		
$2KI$	+	Cl_2	=	$2KCl$	+	I_2
Potassium iodide.		Chlorine.		Potassium chloride.		Iodine.
$2KI$	+	$2NO_2$	=	$2KNO_2$	+	I_2
Potassium iodide.		Nitrogen tetroxide.		Potassium nitrite.		Iodine.

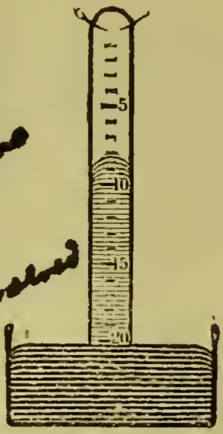
So that the best test for ozone in the air will evidently depend, not on the liberation of iodine from iodide of potassium, since both chlorine and nitrogen tetroxide can effect this, but on ascertaining whether, with the liberation of the iodine, the solution of iodide of potassium becomes alkaline, since both chlorine and nitrogen tetroxide in liberating the iodine from iodide of potassium leave the solution neutral. The method of applying this modified and improved test for ozone in the air consists in exposing a solution of iodide of potassium coloured with red litmus to the air, for some hours, in a shallow vessel, when, if ozone is present, the red colour changes to blue; whereas if chlorine or nitrogen tetroxide are present in the air, although they liberate the iodine from the iodide of potassium, yet the chloride of potassium and nitrite of potassium respectively formed, being neutral, are incapable of changing the colour of the red litmus.

3 vols of O condensed to two.

That ozone consists of oxygen condensed in the ratio of three volumes to two can be shown by the following experiment:—

Some pure oxygen is enclosed, over mercury, in a graduated glass tube furnished with platinum wires and open at the bottom. Say, 100 volumes of oxygen are taken, sparks are passed through the gas and

100 is now 97.
i.e. 3 vols of O_2 have disappeared.
99 became 97 with tps. added
i.e. 2 vols of O_3 dissolved
of O_2.
= 3 of
2 of O_3



100
Contract^n
99.
after turpentine passed up.
97.

Fig. 8.—Constitution of Ozone.

the volume contracts, ozone being formed, to ninety-nine. Turpentine is then passed up into the mixed gases to dissolve out all the ozone. The volume is now ninety-seven. The total quantity of oxygen converted into ozone is therefore 100 — 97 = 3 vols., and the ozone (as shown by the absorption with turpentine) is 99 — 97 = 2 vols. In other words, three volumes of O_2, when converted into O_3, only occupy two volumes.

Preparation & properties of Carbo
of Hydrogen with Oxygen ?

CHAPTER III.

WATER—HYDROGEN DIOXIDE.

Water — Composition — Properties — Water of Crystallisation — Efflorescence —Deliquescence—Sources of Drinking Waters—Soft and Hard Waters —Temporary and Permanent Hardness—River and Mineral Waters—Solvent Action of Water—Hydrogen Dioxide—Modes of Preparation—Test for Hydrogen Dioxide.

WATER.

Formula, H_2O ; *molecular weight*, 18.

Composition of H_2O: By Volume.

Composition.—Water is composed of hydrogen and oxygen united in the proportion of two parts of hydrogen by weight to sixteen of oxygen, or, by volume, it is formed by the union of two volumes of hydrogen with one volume of oxygen. The composition of water may be proved in the following ways : ?

(i) *The analytical method.*—By electrolysis or the decomposition of water into its elements by means of a current of electricity (see page 74).

(ii) *The synthetical method.*—(*a*) By introducing a mixture of two parts by volume of hydrogen to one of oxygen into a eudiometer, and then exploding the mixture by means of an electric spark, when water will be formed. This may be effected in the Cavendish A eudiometer (Fig. 9, A), which consists of a stout glass vessel, provided with a stop-cock at the lower part, and with two platinum wires fused through the glass at the upper part. The eudiometer is first exhausted of air by means of an air-pump, and is then filled with a mixture of two volumes of hydrogen to one volume of oxygen by connecting it with a bottle (B) containing the two gases in those proportions ; the stop-cock is closed and the eudiometer detached from B; the gases may then be exploded by means of an electric spark between the two platinum wires, the electricity being furnished by a charged Leyden jar (C). By the explosion of the hydrogen and oxygen

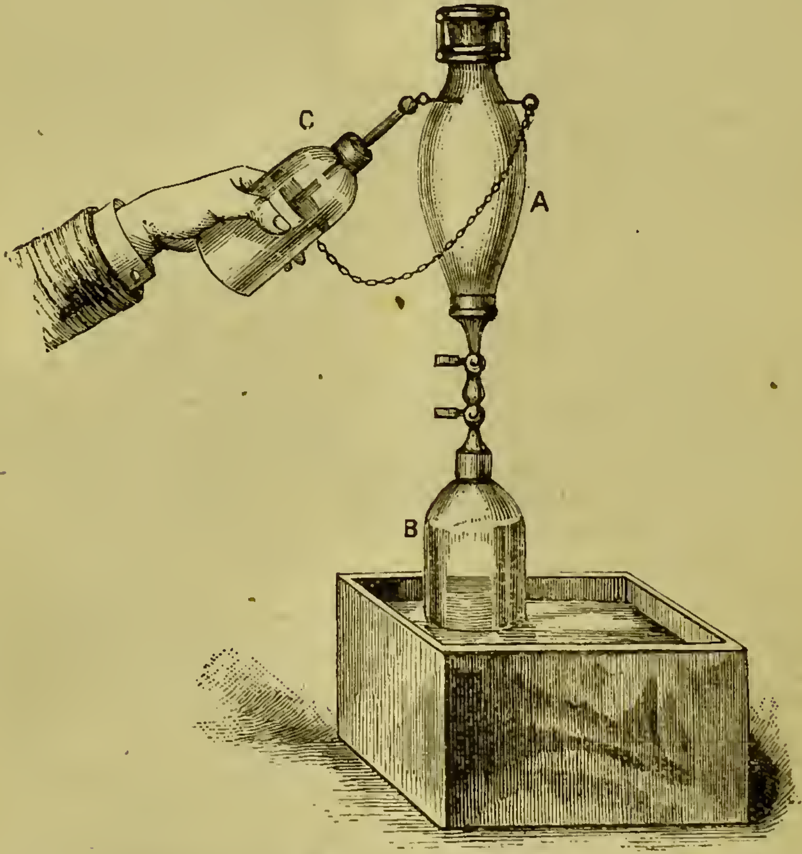


Fig. 9.—Formation of Water by the Explosion of Hydrogen and Oxygen in the Cavendish Eudiometer.

water will be formed, and will be deposited as a film upon the inner surface of the eudiometer, and the complete conversion of these two gases into water will be demonstrated by the fact that, on opening the stop-cock of the eudiometer under water, the interior of it will be immediately and completely filled by the water, on account of the vacuum left within the eudiometer by the union of the hydrogen and oxygen, and the condensation of the resulting water as a film on the inner surface of the vessel.

2. A more instructive form of this experiment is that devised by Hofmann (Fig. 10). A U-shaped tube A, closed at one end and open at the other, is partly filled with a mixture of two volumes of hydrogen and one volume of oxygen, the gases being enclosed by mercury in the bend of the tube. The closed limb A of the U-tube is furnished with two platinum wires at its upper end and is graduated. It is surrounded by a second tube B, through which passes a stream of vapour from the boiling amylic alcohol in the flask. By this means the tube A is kept at a temperature of 130°, well above the boiling-point of water. As soon as the expansion produced by the heating of the gases by the boiling alcohol vapour has ceased, the open end of the tube is temporarily closed by a cork, and the gases exploded by passing a spark between the platinum wires. On removing the cork and levelling the mercury, it will be seen that the three volumes of H and O have condensed to two volumes of steam, and if the stream of hot vapour be stopped, these two volumes of steam will condense to a minute drop of water, and the mercury will rise to the top of the tube.

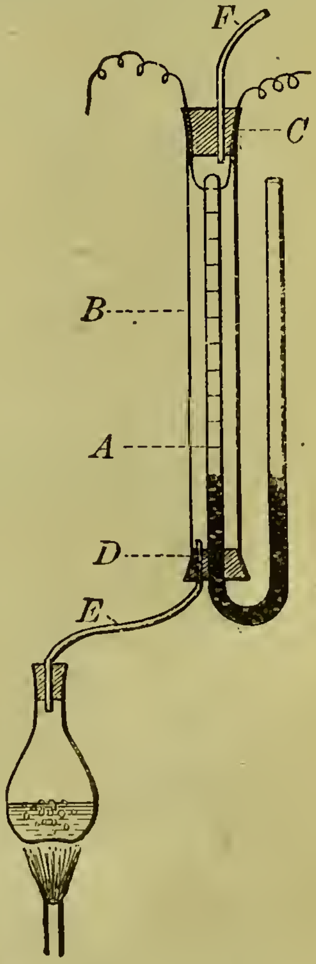


Fig. 10.—Hofmann's Experiment.

ition of H_2O
by weight

(b) The composition of water by weight was proved by Dumas in 1843 by passing pure dry hydrogen over a known weight of oxide of copper contained in a bulb, and heated to redness. The hydrogen unites with the oxygen of the oxide of copper to form water, and so reduces the oxide to the condition of metallic copper.

$$\underset{\text{Copper oxide.}}{2CuO} + \underset{\text{Hydrogen.}}{2H_2} = \underset{\text{Copper}}{2Cu} + \underset{\text{Water.}}{2H_2O}$$

The water, which passes away from the tube in the form of steam, may be collected in a previously-weighed chloride of calcium tube, the increase in weight of which at the end of the experiment will give the amount of water produced, while the loss of weight of the copper oxide will give the weight of oxygen.

Properties.—Pure water in thin layers is a colourless liquid, but if viewed through a tube six feet in length. which is filled with it, and which is blackened at the sides and provided with glass ends, it is then seen to possess a faint blue colour—a colour that is also well seen in glacier ice, in deep sea-water, and in the Croydon swimming bath, where the water from deep chalk wells is used. The presence of a very small amount of animal organic matter (sewage), or of vegetable organic matter (peat), will cause the blue colour of the water to be replaced by a yellow or brownish tint. Pure water is tasteless and odourless; its specific gravity is 1, that is, it is chosen as the standard with which the weights of equal volumes of all other liquids and solids are compared; it freezes at 0° C., and boils at 100° C., under the normal atmospheric pressure. A large number of solids and gases are capable of passing into the liquid state when placed in water, *i.e.* they are **soluble** in the water. Some liquids, such as alcohol and glycerin, are

miscible with water in all proportions; others, such as chloroform and ether, only in small proportions; and others, such as olive oil and castor oil, not at all. Many solid chemical substances are capable of forming a loose chemical union with water, which in this solid form is then known as **water of crystallisation.** *Examples.*—Sodium carbonate (Na_2CO_3, $10H_2O$), zinc sulphate ($ZnSO_4$, $7H_2O$), copper sulphate ($CuSO_4$, $5H_2O$).

Water of crystallisation is capable of being expelled or driven off by heat, but there are some crystalline bodies that slowly part with their water of crystallisation by simple exposure to the air. This phenomenon of the spontaneous loss of water of crystallisation on exposure to the air is known as **efflorescence,** and such bodies are called **efflorescent** (from *efflorescens*, blossoming forth), on account of their assuming a powdery condition; for instance, ordinary washing soda (Na_2CO_3, $10H_2O$) is a good example of an efflorescent body, crystals of it, on exposure to dry air, losing their water of crystallisation, and becoming opaque and powdery. On the other hand, **deliquescence** is the power possessed by certain solid substances of absorbing moisture from the air to such an extent as to become moist and finally liquid, from the solid dissolving in the absorbed water; such bodies are called **deliquescent** (from *deliquescens*, melting away), on account of the liquefaction that they undergo on exposure to the air; calcium chloride and potassium carbonate are two good examples of deliquescent substances, as they soon become liquid on exposure to the air.

Sources and varieties of water as used for drinking purposes.—Rain and snow are the natural sources from which drinking waters are derived. Rain when it falls upon the surface of the earth is disposed of in three ways: (1) part of it is returned to the atmosphere by evaporation; (2) part of it flows according to the inclination of the surfaces, and so contributes to the formation of brooks, streams, and rivers; (3) part of it sinks or percolates into the soil until it reaches an impermeable stratum of hard rock or clay, and so forms the underground sources of water that are made available for the use of man either by coming to the surface as springs, or by being tapped by the sinking of wells or pumps.

Rain-water as it leaves the clouds is pure, but in its passage through the air it may absorb and collect many substances, such as oxygen, carbon dioxide, traces of ammonia, sulphur dioxide, nitrogen tetroxide, chlorine, sodium chloride (if in the vicinity of the sea), particles of soot, and various fungoid and bacterial organisms. The rain-water percolating through, or flowing over, the soil may dissolve from it various substances, such as lime salts, magnesia salts, etc. Rain-water is a very soft water, and is therefore useful for washing purposes. A **soft water** is one in which soap can dissolve, and therefore readily form a lather without being precipitated; a **hard water**, on the other hand, is one in which soap, as fast as it dissolves, is precipitated by some substance or substances present in the water, and so the formation of a lather is rendered difficult. The hardness of a water is caused by the presence of calcium and magnesium salts and may be temporary or permanent, or a combination of the two; **temporary hardness** is that which can be removed by boiling the water, and is due to the presence of the soluble bicarbonates of calcium and magnesium, which on boiling are converted into the insoluble carbonates of those metals, and these being deposited constitute the *fur* that accumulates in kettles and boilers. Temporary hardness is acquired by rain or stream water, containing carbon dioxide in solution, flowing over some form of calcium carbonate (chalk or limestone), or magnesium carbonate in the soil; such water containing carbon dioxide in solution is capable of forming a soluble bicarbonate with either of these carbonates, thus:

$$\begin{array}{ccccccc} CaCO_3 & + & CO_2 & + & H_2O & = & Ca(HCO_3)_2 \\ \text{Calcium} & & \text{Carbon} & & \text{Water.} & & \text{Calcium} \\ \text{carbonate.} & & \text{dioxide.} & & & & \text{bicarbonate.} \end{array}$$

This soluble bicarbonate loses part of its carbon dioxide on boiling, and the insoluble calcium carbonate is once more formed and deposited, thus:

$$\begin{array}{ccccccc} Ca(HCO_3)_2 & = & CaCO_3 & + & CO_2 & + & H_2O \\ \text{Calcium} & & \text{Calcium} & & \text{Carbon} & & \text{Water.} \\ \text{bicarbonate.} & & \text{carbonate.} & & \text{dioxide.} & & \end{array}$$

Permanent hardness is that which cannot be removed by boiling, and is generally due to the presence of calcium or magnesium sulphate. In the case of sea-water the hardness is due to sodium chloride, which renders ordinary soap insoluble (*see* ORGANIC CHEMISTRY, Chap. VIII.). The difficulty experienced with a hard water of obtaining a lather with ordinary soap (sodium oleate) is thus explained: as soon as some of the soap dissolves, it is converted into the insoluble calcium or magnesium oleate, and not until all the calcium salts are thus precipitated do we get a solution of soap which forms the lather. The use of hard water, therefore, entails great waste of soap. Water can be softened, if it is only to be used for washing purposes, by adding a little sodium carbonate, when all the calcium and magnesium salts will be precipitated as carbonates, and after allowing these to subside the clear water will be quite soft. Another process, which is applicable to drinking water and is known as Clark's process, consists in adding a weighed quantity of slaked lime to a known bulk of the water, when the whole of the lime added and the lime to which the temporary hardness is due are precipitated. The reaction is represented by the equation :

$$\begin{array}{ccccccc} \left\{\begin{matrix} CaCO_3 \\ H_2CO_3 \end{matrix}\right. & + & Ca(HO)_2 & = & 2CaCO_3 & + & 2H_2O \\ \text{Calcium bicarbonate.} & & \text{Slaked lime.} & & \text{Chalk.} & & \text{Water.} \end{array}$$

It will be noticed that one molecule of calcium hydrate is required to precipitate one molecule of the bicarbonate.

The best method of purifying water is by distillation, when all the solid impurities are left behind in the still. The first and last portions of the distillate should be rejected.

The principal constituents of three typical river waters are given below. The Dee, which flows over hard insoluble rocks, slates, etc., is a typical soft water ; the Thames, which cuts through the chalk and has much temporary hardness ; and the Trent, which contains much calcium sulphate and sodium chloride :

	Thames.	Trent.	Dee.	
Calcium carbonate	10·8	0·32	0·85	grs. per gal.
Calcium sulphate	3·0	21·55	0·12	„
Salt	1·8	17·63	0·72	„
Organic matter	2·36	3·68	1·54	„

Sea water contains 3 to 4 per cent. of salts, chiefly sodium chloride (1,850 grains per gallon) and magnesium salts.

Drinking water is purified by filtration through beds of sand and gravel, during which process much of the organic matter is oxidised, probably by the combined action of bacteria and the oxygen of the air.

Mineral waters.—These are spring waters containing in solution some medicinal ingredient. In the following table the more important mineral waters are enumerated, with their sources and composition :

SOURCE.	COMPOSITION.
Vichy Carlsbad Ems Seltzer Malvern Apollinaris	Alkaline waters, containing sodium carbonate and bicarbonate; effervescence due to carbon dioxide.
Spa Tunbridge Some Cheltenham Waters.	Chalybeate waters, containing ferrous carbonate held in solution by excess of carbon dioxide.
Harrogate Aix-la-Chapelle	Sulphuretted waters, containing free sulphuretted hydrogen.
Leamington Epsom	Aperient saline waters, containing magnesium sulphate.
Cheltenham Scarborough	Aperient saline waters, containing sodium sulphate and sodium chloride.
Bath Bristol Matlock	Calcareous waters, containing calcium bicarbonate and calcium sulphate.

Solvent action of water.—Many substances are soluble in water. As a rule, boiling water dissolves a larger quantity of a solid substance than cold water. When water has dissolved the maximum quantity of a substance, the solution is said to be "saturated." If a saturated solution be made at the boiling-point and the solution be allowed to cool, the excess dissolved at the boiling-point over the quantity dissolved at the ordinary temperature, separates out, usually in crystals. This process is largely used in purifying substances by "recrystallisation." One notable exception to the above rule is common salt, which dissolves almost as readily in cold as in hot water. Some of the calcium compounds ($Ca(HO)_2$ and $CaSO_4$) are slightly more soluble in cold than in hot water.

The solubility of *gases* in water depends (1) upon the nature of the gas, thus 1,000 vols. of ammonia dissolve in 1 vol. of water, while only ·02 vol. of hydrogen dissolve in 1 vol. of water; (2) on the temperature, the lower the temperature of the water the greater is the volume of the gas dissolved—in most cases ice and boiling water contain no dissolved gases; (3) on the pressure, the greater the pressure the greater is the volume dissolved; if you double the pressure twice as much gas is dissolved.

HYDROGEN DIOXIDE.

Peroxide

Oxygenate Water

Formula, H_2O_2; *molecular weight*, 34.

Water and hydrogen dioxide constitute the two oxides of hydrogen. Hydrogen dioxide is also known as peroxide of hydrogen, and as oxygenated water, the latter name being given to it on account of the facility with which it decomposes into water and oxygen.

Modes of preparation.—(i) Hydrogen dioxide may be obtained by the action of any dilute acid on barium dioxide. Thus, if diluted hydrochloric acid be added to barium dioxide, double decomposition takes place, barium chloride and hydrogen dioxide being formed:

HCl

BaO_2	+	$2HCl$	=	$BaCl_2$	+	H_2O_2
Barium dioxide.		Hydrochloric acid.		Barium chloride.		Hydrogen. dioxide.

Hydrochloric acid, however, is not a convenient acid to use in the preparation of hydrogen dioxide, since this latter body is contaminated by the presence

℞ $BaO_2 + HCl$ in HCl

of the soluble barium chloride. It is therefore preferable to select an acid which will yield an insoluble barium salt, and so leave only the hydrogen dioxide in solution; carbonic acid answers these requirements admirably. If carbon dioxide be passed through water containing barium dioxide suspended in it, carbonate of barium is precipitated and a pure solution of hydrogen dioxide obtained:

$$\underset{\text{Barium dioxide.}}{BaO_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon dioxide.}}{CO_2} = \underset{\text{Barium carbonate.}}{BaCO_3} + \underset{\text{Hydrogen dioxide.}}{H_2O_2}$$

(ii) Hydrogen dioxide is said to be obtained as one of the products of the atmospheric oxidation of several of the natural volatile oils in presence of moisture, such as the oils of turpentine, pine, eucalyptus, etc.

Properties.—Hydrogen dioxide is a syrupy liquid, but is usually obtained mixed with water, a 10 or 20 per cent. solution being the usual strength of the commercial article. It is colourless and odourless, but possesses an astringent taste, and is miscible with water in all proportions. Its special property consists in the readiness with which it splits up into water and oxygen:

$$\underset{\text{Hydrogen dioxide.}}{2H_2O_2} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{O_2}$$

This decomposition may be brought about by boiling, or by bringing it in contact with bodies in want of oxygen, when the hydrogen dioxide readily parts with one-half of its oxygen; it is in this way that it acts as a disinfectant and deodoriser. Hydrogen dioxide is also a powerful bleaching agent by virtue of its power of rapidly oxidising colouring matters, and so bleaching them; its effect as a so-called hair-dye, in

$Na_2O_2 + 2HCl = 2NaCl + H_2O_2$

$Cr-O_3$

turning the hair yellow or white, is simply that of a bleaching agent.

Test.—Hydrogen dioxide possesses the property of liberating iodine from iodide of potassium, the liberated iodine turning starch solution blue; this is a property, however, possessed by other substances, but unlike all these other oxidising agents, hydrogen dioxide will liberate the iodine from iodide of potassium in presence of ferrous sulphate.

If hydrogen dioxide be poured on some black oxide of manganese, an effervescence takes place, owing to the escape of oxygen. This enables us to test the strength of a solution of peroxide of hydrogen by measuring the volume of oxygen evolved. When peroxide of hydrogen is mixed with chromic acid and a little ether, the ether is coloured a beautiful blue colour, owing to the formation of perchromic acid, $HCrO_4$.

H₂

H_2O P_2O_5

Isolation & Characters of Nitrogen.

CHAPTER IV.

NITROGEN—THE ATMOSPHERE.

Nitrogen — Preparation and Properties of Nitrogen — Test for Nitrogen—Composition of the Atmosphere—Methods of determining the Composition of the Atmosphere—Proofs that the Atmosphere is a Mixture, and not a Compound, of Oxygen and Nitrogen—Aqueous Vapour in the Air—Carbon Dioxide in the Air—Ozone in the Air—Impurities in Air.

NITROGEN.

Symbol, N ; *molecule*, N_2 ; *pentad* (also capable of acting as a *triad*, *monad*, *etc.*, *see* page 30) ; *atomic weight*, 14 ; *molecular weight*, 28 ; *liquefies at* —194°.

NITROGEN (meaning *generator of nitre*) owes its name to the fact that it is an essential constituent of nitre (nitrate of potash). Nitrogen is widely and extensively distributed in nature ; it constitutes four-fifths of the bulk of the atmosphere, it is present in all natural nitrates, and forms an important constituent of the tissues and organs of all animals and plants ; in animals it is present in albumin, fibrine, cartilage, casein, urea, etc. ; in plants it is present in vegetable albumin and in all alkaloids.

Modes of preparation.—(i) Nitrogen may be obtained by removing the oxygen from a limited volume of air by any of the following processes :—

(*a*) By burning phosphorus under a bell-jar standing over water ; the phosphorus consumes all the oxygen of the air contained in the bell-jar, forming a white powder—phosphorus pentoxide (P_2O_5)—which dissolves in the water, forming phosphoric acid (H_3PO_4), and the space formerly occupied by the

from Ai

$_2O_5 + 3H_2O = 2H_3PO_4$

oxygen is filled by the water taking its place. The gas within the bell-jar now occupies four-fifths of the original volume of the air taken, and consists of nitrogen.

(b) By absorbing oxygen from a confined volume of air by means of a solution of pyrogallate of potassium.

pure dry.

(c) By passing air over red-hot copper turnings contained in a long porcelain tube, when the copper unites with the oxygen of the air to form copper oxide (CuO), and pure nitrogen passes on. This reaction is much facilitated by adding a little ammonia (NH_3) to the air.

(d) By exploding in a eudiometer 42 volumes of hydrogen with 100 volumes of air (the latter containing just 21 volumes of oxygen), when the hydrogen and oxygen will unite to form water, which will condense on the sides of the eudiometer, and nitrogen will remain.

(ii) Nitrogen may be very readily obtained by boiling together solutions of potassium nitrite and ammonium chloride, when double decomposition between the two salts first takes place, resulting in the formation of ammonium nitrite and potassium chloride.

$$\underset{\text{Potassium nitrite.}}{KNO_2} + \underset{\text{Ammonium chloride.}}{NH_4Cl} = \underset{\text{Ammonium nitrite.}}{NH_4NO_2} + \underset{\text{Potassium chloride.}}{KCl}$$

The ammonium nitrite then splits up into nitrogen and water.

$$\underset{\text{Ammonium nitrite.}}{NH_4NO_2} = \underset{\text{Nitrogen.}}{N_2} + \underset{\text{Water.}}{2H_2O}$$

(iii) Nitrogen may also be prepared by passing chlorine into solution of ammonia, when ammonium chloride is formed and nitrogen evolved.

N – the chloro-[illegible] [illegible] in the animal kingdom [illegible] vegetable

$$\underset{\text{Ammonia.}}{8NH_3} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Ammonium chloride.}}{6NH_4Cl} + \underset{\text{Nitrogen.}}{N_2}$$

In this process care must be taken to keep the ammonia in excess, otherwise the chlorine would act upon the ammonium chloride, forming the terribly explosive chloride of nitrogen.

Properties.—The specific gravity of nitrogen is 14, and it is a little lighter than air. The properties of nitrogen are mainly negative; it is odourless, tasteless, colourless, not combustible, a non-supporter of combustion, and but slightly soluble in water; it is not poisonous, since the air contains about four-fifths of it by volume, but it is incapable of supporting life by itself. The main function of the nitrogen of the atmosphere is to dilute down the oxygen, which would otherwise be too energetic in its action.

Test.—A lighted taper, if plunged into a jar of nitrogen, is immediately extinguished, and the gas itself does not ignite. The only other odourless, or comparatively odourless, gas that behaves in this way is carbon dioxide, and the two may be readily distinguished by carbon dioxide turning lime-water milky, whereas nitrogen has no effect upon lime-water. So that the combined facts of an odourless gas extinguishing a lighted taper, being non-combustible, and not turning lime-water turbid, will indicate that the gas is nitrogen.

Generally [illegible] [illegible] [illegible] brought [illegible] for the [illegible] this.

THE ATMOSPHERE.

Specific gravity = 14·4 (H = 1).

The atmosphere mainly consists of a mixture of oxygen and nitrogen in the following proportions:—

	By volume.	By weight.
Oxygen	21	23
Nitrogen	79	77

Other bodies, however, are, or may be, present in the air in small quantities. In the following list are enumerated all the possible constituents of the atmosphere divided into three groups: 1, the principal constituents; 2, essential constituents; and 3, occasional constituents of the atmosphere.

21 Oxygen 79 Nitrogen	Principal constituents of the atmosphere.
Water (in the form of aqueous vapour, clouds or mists) Carbon dioxide	Other essential constituents of the atmosphere.
Ozone Nitrogen tetroxide and nitric acid Sulphur dioxide and sulphurous and sulphuric acids Chlorine Sulphuretted hydrogen Argon Carbonic oxide Particles of soot Fungoid and bacterial organisms	Constituents that are or may be present in the atmosphere in small quantities.

In describing the chemistry of the atmosphere, it will be convenient to discuss separately the constituents of the air, in the order above given in the three divisions.

1. **The principal constituents of the atmosphere—oxygen and nitrogen.**—As previously stated, oxygen and nitrogen so nearly make up the entire bulk of the atmosphere that, in indicating the percentage composition of the air, it is customary to make the percentages of these two gases add up to 100, although actually a small fraction of the percentage composition should be reserved for the other constituents of the air.

— **Methods of determining the composition of the atmosphere.**—(*a*) *The eudiometric method.*

—By this method the amount of oxygen in the air is determined by observing the contraction that takes place after exploding a known volume of air in a eudiometer with excess of hydrogen; since two volumes of hydrogen unite with one volume of oxygen to form water, one-third of the contraction will be due to oxygen, and so the proportion of oxygen present in the known volume of air will be ascertained.

(*b*) *Pyrogallate of potassium method.*—This consists in exposing a measured volume of air, contained in a graduated tube standing over mercury, to the action of a strong solution of pyrogallate of potassium, which possesses the property of absorbing oxygen from the air; at the end of an hour the diminution in volume of the air is noted, and this represents the amount of oxygen contained in the measured volume of air originally taken.

(*c*) *The copper method.*—In this process a previously-weighed tube containing copper turnings is raised to a red heat, and a known weight of air is then passed through it; the copper unites with the oxygen of the air, forming oxide of copper, and the nitrogen may be allowed to pass on into a glass globe provided with a stop-cock, which has been previously exhausted of air at the air-pump and then weighed; at the end of the experiment the increase in weight of the tube containing the copper turnings will give the amount of oxygen contained in the weighed quantity of air experimented with, while the increase in weight of the previously exhausted globe will give the amount of nitrogen.

(*d*) *The synthetical method.*—This consists in mixing together oxygen and nitrogen in the proportion of 21 volumes of oxygen to 79 volumes of nitrogen, when a mixture possessing all the properties of air will be obtained.

prove Air. a mixture

5 Proofs ✓

The atmosphere a mixture of oxygen and nitrogen, not a compound of those gases.—That the atmosphere is simply a mechanical mixture of oxygen and nitrogen, and not a chemical compound of those two gases, may be proved in various ways.

(*a*) *By the method of mixture.*—This consists, as just described, in mixing together 21 volumes of oxygen with 79 volumes of nitrogen, when no heat is evolved or absorbed; neither is there any change of volume or colour, in fact there is no sign of any chemical action, and yet the resulting mixture possesses all the physical and chemical properties of air.

(*b*) *By solution in water.*—Dissolved air is different in composition to ordinary air; if the air were a chemical compound of oxygen and nitrogen, then mere solution in water would be unable to alter its composition, whereas if it be a mixture of the two gases, then, on account of the greater solubility of oxygen in water as compared with nitrogen, the dissolved air should be richer in oxygen than ordinary air; this is actually the case.

If air be well agitated with water, and then the dissolved gas expelled by boiling the water and collected in a tube, it will be found on making an analysis of this dissolved gas that it contains more oxygen than ordinary air, as shown in the following table:—

	Composition by volume of	
	Ordinary air.	Dissolved air.
Oxygen	21	35
Nitrogen	79	65

(*c*) *By the diffusion experiment.*—If the air were a chemical compound of oxygen and nitrogen, then on submitting it to the process of diffusion it would

NO [illegible] [illegible] [illegible] [illegible]
O. It does so with air and not with any other
compounds [illegible] O in the combination

diffuse unchanged in composition, since by diffusion ~~alone it is impossible to separate~~ the constituents of ~~gaseous~~ chemical compounds; but if it be a mechanical ~~mixture~~ of oxygen and nitrogen, then on submitting it to diffusion the relatively lighter gas nitrogen should diffuse at a greater rate than the heavier oxygen (*see* Graham's "Law of Diffusion, page 70), and this is actually what does take place.

Fig. 11 represents the diffusion apparatus for proving that the atmosphere is a mechanical mixture of oxygen and nitrogen.

A is a porous tube, consisting of unglazed porcelain, passing through two perforated india-rubber corks, D

[illegible] we N
[illegible] O diffuse
[illegible] into the vacuum
surrounding D air

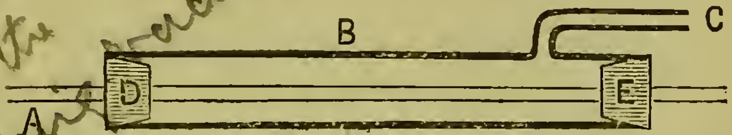


Fig. 11.—Diffusion Apparatus for proving Air to be a Mixture of Oxygen and Nitrogen.

and E; B is a stout glass tube fitting tightly over the corks D and E, and provided with an arm or outlet, C, by which it can be connected with an air-pump. By this means it is possible to produce a vacuum in B, and around that portion of the porous tube, A, lying between the corks D and E; if, now, air be passed through A it will tend to diffuse through the porous tube into the vacuum in B, and on examining this air which has diffused through into B it will be found to be richer in nitrogen than ordinary air, owing to the lighter nitrogen having diffused through the pores of the tube A at a greater rate than the heavier oxygen; this separation by diffusion could only take place from a mechanical mixture of the two gases, and not from a chemical compound.

(*d*) The relative weights of nitrogen and oxygen in the air are not simple multiples of their atomic weights 14 and 16.

(e) The composition of the air is not quite constant.

2. **Essential constituents of the atmosphere other than oxygen and nitrogen.** (a) *Aqueous vapour.*—This is derived by evaporation from large masses of water, such as the sea, lakes, rivers, etc.; from the respiration of human beings and animals; by evaporation from the skin; and by evaporation from plants. This aqueous vapour of the air, by condensing to small particles of water, forms clouds and mists, and by further condensation to actual drops of water produces rain; if when in the fine state of condensation it be frozen, snow is produced; whereas if rain be frozen during its transit to the earth, hail is produced.

The detection of aqueous vapour and the estimation of its amount in the air are effected by passing a measured volume of the air through a previously-weighed chloride of calcium tube, when any aqueous vapour in the air will be readily absorbed by the fragments of chloride of calcium, and the increase in weight of the tube at the end of the experiment will indicate the amount of aqueous vapour in the volume of air employed. The estimation of the amount of aqueous vapour is, however, more usually effected by physical methods, by determining the "dew point."

(b) *Carbon dioxide.*—This gas, commonly known as carbonic acid gas, must be regarded as one of the essential constituents of the air on account of the extremely important part it takes in the maintenance of vegetable life (*see* page 78), although, if allowed to accumulate in excessive quantities, it becomes an impurity of the atmosphere. It is derived from the respiration of human beings and animals, and from the combustion of fuel. The amount of carbon dioxide normally present in the air is very small, being 4 parts in 10,000 or ·04 per cent., and an amount slightly in excess of this in the air of inhabited rooms must be regarded as an impurity, not so much on account of the carbon dioxide itself, as because it is derived from the respiration of human beings, and in the air exhaled from the lungs, putrefiable organic matters are present that have a decidedly deleterious effect on the health of human beings breathing such air. When the carbon dioxide in the air of an inhabited room exceeds ·06 per cent., these putrefiable organic matters become noticeable by smell, rendering the air stuffy or foul, but since these organic matters are extremely difficult to estimate, the determination of the amount of carbon dioxide present becomes a useful gauge of the foulness of the air. If the carbon dioxide be pure 3 per cent. may be present without producing inconvenience. To detect carbon dioxide in the air, all that is necessary is to expose some lime-water to the atmosphere, when the presence of carbon dioxide is indicated by the lime-water becoming turbid or milky, owing to the precipitation of carbonate of lime. To estimate the amount of carbon dioxide in the air, a half-gallon bottle is filled with the air to be examined, and a measured quantity of baryta-water is poured into the bottle and thoroughly agitated with the air in it. The strength of the baryta-water is previously determined by ascertaining how much of a standard solution of oxalic acid is required to neutralise the same quantity of baryta-water as that introduced into the half-gallon bottle. If now the measured quantity of baryta-water that has been agitated with the half-gallon of air be filtered from the precipitated carbonate of barium, and its strength be determined by noting the quantity of standard acid that is required to neutralise it, it will be found to be deficient in a certain amount of baryta, which represents the quantity of baryta precipitated by the carbon dioxide in the half-gallon of air, from which the amount of carbon dioxide present in the air can be easily calculated.

3. Other substances that may be present in the atmosphere. *Ozone.*—This gas is present in minute quantities in country air and in the vicinity of the sea, but not, as a rule, in the atmosphere of towns. Its production in the air, and the means of detecting it, have been previously described (*see* pages 80, 81).

Impurities. (*a*) *Nitrogen tetroxide and nitric acid.*—These are mainly derived from chemical works and factories. Small quantities of nitrogen peroxide may be formed by direct union of the nitrogen and oxygen of the air during a thunderstorm, the nitrogen peroxide subsequently uniting with the moisture in the air to form nitrous and nitric acids.

$$\underset{\substack{\text{Nitrogen}\\\text{peroxide.}}}{2NO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Nitrous}\\\text{acid.}}}{HNO_2} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{HNO_3}$$

(*b*) *Sulphur dioxide and sulphurous and sulphuric acids.*—Derived from the combustion of sulphur in coal, and from chemical works and factories.

(*c*) *Chlorine.*—From bleaching powder and other chemical works.

(*d*) *Sulphuretted hydrogen.*—Produced in the manufacture of coal gas, etc.

(*e*) *Carbon dioxide in excess.*—A product of respiration, combustion of coal, etc.

(*f*) *Carbonic oxide.*—From imperfect combustion of fuel.

(*g*) *Particles of soot.—See f.*

(*h*) *Fungoid organisms and bacteria.* — From various sources

In 1894 Lord Rayleigh and Professor Ramsay discovered a new element in the atmosphere which they named Argon; its atomic weight is either 20 or 40, it is the most inactive element known, as it refuses to combine with anything; it occurs in the atmosphere to the extent of about 0·9 per cent.; curiously enough, it was isolated by Cavendish in 1785, but he failed to recognise it as a new element. It is a colourless gas, very much like nitrogen, and liquefies at —187°.

mpounds of Nitrogen with Oxygen?

CHAPTER V.

OXIDES OF NITROGEN—NITRIC ACID.

Nitrogen Monoxide — Nitrogen Dioxide — Nitrogen Trioxide — Nitrogen Pentoxide—Modes of Preparation and Properties of the Oxides of Nitrogen—Tests for the Oxides of Nitrogen—Nitrous Acid—Nitric Acid—Nitrates.

THE OXIDES OF NITROGEN.

THERE are five compounds of oxygen and nitrogen, viz. :

hyponitrous anhy

N_2O	Nitrogen monoxide, or nitrous oxide, or laughing gas.
NO	Nitrogen dioxide or nitric oxide.
N_2O_3	Nitrogen trioxide or nitrous anhydride.
NO_2	Nitrogen tetroxide or nitric peroxide.
N_2O_5	Nitrogen pentoxide or nitric anhydride.

Of these oxides, the first four mentioned are gases, the last is a white crystalline solid. The first two (N_2O and NO) are colourless gases, the second two (N_2O_3 and NO_2) are both of a reddish-brown colour.

The chemistry of the individual oxides of nitrogen will be now considered.

NITROGEN MONOXIDE.

Formula, N_2O; *molecular weight*, 44; *liquefies at* −90°.

Also known as *nitrous oxide* and *laughing gas*.

Mode of preparation.—Nitrous oxide is obtained by heating crystals of ammonium nitrate in a flask, and collecting the gas over warm water, as it is appreciably soluble in cold water (Fig. 12).

$$\underset{\text{Ammonium nitrate.}}{NH_4NO_3} = \underset{\text{Nitrous oxide.}}{N_2O} + \underset{\text{Water.}}{2H_2O.}$$

heat

Properties.—The specific gravity of nitrous oxide is 22, and it is heavier than air; it is colourless and odourless, but has a slightly sweet taste; it is non-combustible; it is fairly soluble in cold water, but considerably less so in hot. It is not a poisonous gas, although when inhaled in a pure state it produces insensibility, and is hence used for the painless performance of some minor operations. If the administration of it be continued for too long a time, death from asphyxia will result. Nitrous oxide, prepared as above, usually contains some nitrogen peroxide and chlorine (the latter from the ammonium chloride usually present in commercial ammonium nitrate). To get rid of these dangerous impurities, the gas should be passed through potassium hydrate and ferrous sulphate solutions. The name of "laughing gas" is due to the fact that if nitrous oxide be inhaled mixed with air, a feeling of exhilaration is

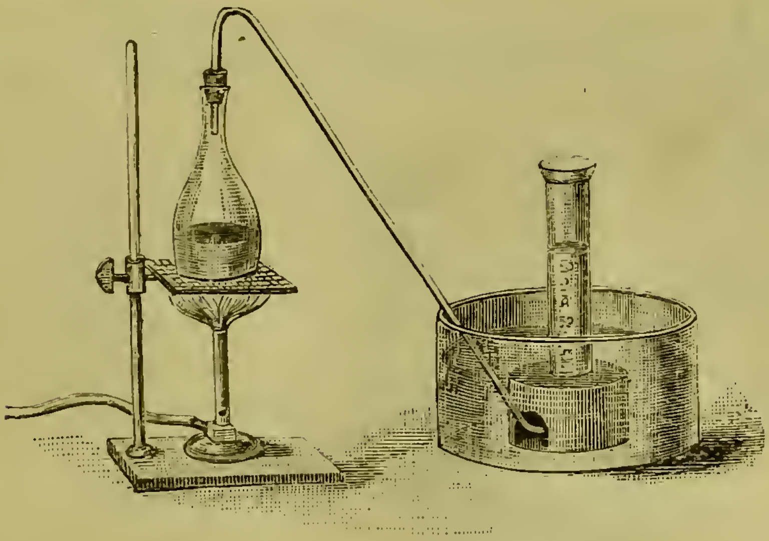


Fig. 12.—Preparation of Nitrogen Monoxide.

produced. Nitrous oxide, when brought in contact with the air, remains unchanged.

Tests.—The fact that nitrous oxide is a colourless gas, and does not change colour on exposure to the air, is sufficient to distinguish it from the other oxides of nitrogen; it may, however, be confounded with oxygen, since it rekindles a glowing splinter of wood. It can be readily distinguished from oxygen by two tests:

add
N

(a) Adding a little nitric oxide, which will produce no effect with nitrous oxide, but will turn deep red with oxygen.

Bur
K

(b) Burning a piece of potassium in some of the gas collected over mercury; nitrous oxide liberates its own volume of nitrogen, and so the volume of the gas when cold will be unchanged; if, however, it is pure oxygen the gas will disappear, as it combines with the potassium to form solid potassium oxide.

Phosphorus and sulphur, when well alight, burn brilliantly in laughing gas.

NITROGEN DIOXIDE.

Formula, NO; *molecular weight*, 30; *liquefies at* −154°.

Action of [illegible] on [illegible]

Also known as *nitric oxide*.

Modes of preparation.—(1) Nitrogen dioxide is most readily obtained by pouring slightly diluted nitric acid (of sp. gr. 1·23) upon copper turnings, and collecting the gas over water (Fig. 13).

Of the nitric acid employed, only one-fourth furnishes the gas, the other three-fourths uniting with the copper to form copper nitrate, thus:

$$\underset{\text{Copper.}}{3Cu} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Copper nitrate.}}{3Cu(NO_3)_2} + \underset{\text{Nitrogen dioxide.}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

HNO_3 + Cu Fe Pb Hg Ag – NO.

(ii) Nitrogen dioxide may also be prepared by the action of nitric acid, of the same strength as just mentioned, on any of the following metals: viz. iron, lead, mercury, silver, and bismuth.

Properties.—The specific gravity of nitrogen dioxide is 15. As the sp. gr. of NO is 15, its molecular weight must be 30, which indicates the formula NO. In this formula nitrogen must act as a dyad,

HNO_3 on Tin

NO_2

Zn

dil HNO_3 on

NH_4.

$NH_4(NO_3)$.

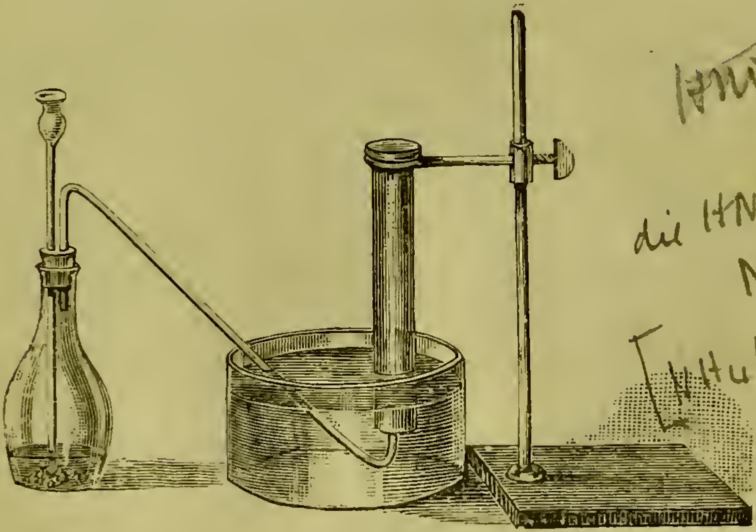


Fig. 13.—Preparation of Nitrogen Dioxide.

which transgresses the usual rule that the valency of an element cannot be odd *and* even; but as the formula is confirmed by the great difficulty of liquefying this gas, which indicates a molecule with fewer atoms than nitrous oxide, the formula NO is given to this substance, and the anomaly as regards the valency of nitrogen awaits future explanation. It is a colourless gas, but on exposure to the air it becomes of a reddish-brown colour, due to its uniting with oxygen of the air to form either nitrogen trioxide or tetroxide. Thus, if in contact with excess of air, nitrogen tetroxide will be produced:

$2NO$	+	O_2	=	$2NO_2$
Nitrogen dioxide.		Oxygen.		Nitrogen tetroxide.

As regards the odour and taste of nitrogen dioxide nothing is definitely known, since it is impossible to either smell or taste it without its being brought into contact with air, in which case the smell and taste of either nitrogen trioxide or tetroxide would be observed. Nitrogen dioxide is non-combustible. A burning taper is extinguished when plunged into this gas, but if a more combustible substance, such as a brightly burning piece of phosphorus, be placed in the gas it decomposes the NO, liberating the oxygen in which it continues to burn. It is practically insoluble in water, and it is a poisonous gas. If passed into a solution of ferrous sulphate it is absorbed, forming a dark brown solution which evolves nitric oxide when heated; advantage is taken of this property in the ordinary test for nitrates, in which ferrous sulphate and sulphuric acid are added as reagents.

Test.—Nitrogen dioxide is the only colourless gas that becomes of a reddish-brown colour on exposure to the air; this is, therefore, a very simple and absolutely diagnostic test for the gas.

NITROGEN TRIOXIDE.

Formula, N_2O_3; *molecular weight*, 76; *liquefies at* −18°.

3 methods.

Also known as *nitrous anhydride*.

Modes of preparation.—(1) Nitrogen trioxide is best prepared by the action of nitric acid, at 70°, on white arsenic (arsenious oxide), when the higher oxide of arsenic is produced, a reddish-brown gas being evolved, thus:

white arsenic + nitric acid.

$_2O_3$ 2HNO_3 H_2O N_2O_3

As_2O_3	+	$2HNO_3$	=	As_2O_5	+	N_2O_3	+	H_2O
Arsenious oxide.		Nitric acid.		Arsenic oxide.		Nitrogen trioxide.		Water.

(ii) Nitrogen trioxide can be obtained, though not in a pure state, by the action of nitric acid, with heat, on starch. $C_6H_{10}O_5$.

(iii) Nitrogen trioxide may also be prepared by bringing nitrogen dioxide in contact with a limited amount of oxygen, or of air, thus:

$4NO$	+	O_2	=	$2N_2O_3$
Nitrogen dioxide.		Oxygen.		Nitrogen trioxide.

Properties.—If the reddish fumes obtained by any of the above reactions be cooled to −18°, a blue liquid is obtained, which is believed to be liquid N_2O_3. There seems to be, however, considerable doubt as to the existence of *gaseous* N_2O_3, the reddish fumes mentioned above being principally a mixture of NO and NO_2. When passed into water the red fumes dissolve, uniting with the water to form nitrous acid, a very unstable body.

N_2O_3	+	H_2O	=	$2HNO_2$
Nitrogen trioxide.		Water.		Nitrous acid.

Similarly, if passed into a solution of an alkali or of an alkaline carbonate, it will form a nitrite of the alkali metal, thus:

$2KHO$	+	N_2O_3	=	$2KNO_2$	+	H_2O
Potassium hydrate.		Nitrogen trioxide.		Potassium nitrite.		Water.
Na_2CO_3	+	N_2O_3	=	$2NaNO_2$	+	CO_2
Sodium carbonate.		Nitrogen trioxide.		Sodium nitrite.		Carbon dioxide.

put into freezing mixture

lead nitrate

NITROGEN TETROXIDE.

Formula, NO_2; *molecular weight*, 46; *liquefies at* +22.

Also known as *nitric peroxide*.

Modes of preparation.—(i) The simplest way of obtaining nitrogen tetroxide, for experimental purposes, is by the action of strong nitric acid on the metal tin, when a violent action takes place with copious evolution of the gas and the production of a white powder, metastannic acid.

$$5Sn + 20HNO_3 = H_{10}Sn_5O_{15} + 20NO_2 + 5H_2O$$

$5Sn$	$20HNO_3$	$H_{10}Sn_5O_{15}$	$20NO_2$	$5H_2O$
Tin.	Nitric acid.	Metastannic acid.	Nitrogen tetroxide.	Water.

(ii) Nitrogen tetroxide may be obtained by mixing nitrogen dioxide with a sufficiency of oxygen, or of air.

$$2NO + O_2 = 2NO_2$$

$2NO$	O_2	$2NO_2$
Nitrogen dioxide.	Oxygen.	Nitrogen tetroxide]

(iii) It is evolved when dry lead nitrate is heated.

or $Hg(NO_3)_2$

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

$2Pb(NO_3)_2$	$2PbO$	$4NO_2$	O_2
Lead nitrate.	Lead oxide.	Nitric peroxide.	Oxygen

Properties.—The specific gravity of nitrogen tetroxide is 23, and it is therefore heavier than air. It possesses a reddish-brown colour, a strong irritating odour, and an unpleasant acid taste. It is non-combustible, and the remarks made on page 110, as to nitrogen dioxide being a supporter of combustion, apply to this gas. It dissolves readily in water, producing a mixture of nitrous and nitric acids.

NO_2 gen

$2NO_2 + H_2O = HNO_3 + HNO_2$

$$\underset{\text{Nitrogen tetroxide.}}{2NO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Nitrous acid.}}{HNO_2} + \underset{\text{Nitric acid.}}{HNO_3}$$

Similarly, if passed into a solution of an alkali or of an alkaline carbonate, it will form a mixture of a nitrite and a nitrate of the alkali metal, thus:

$$\underset{\text{Potassium hydrate.}}{2KHO} + \underset{\text{Nitrogen tetroxide.}}{2NO_2} = \underset{\text{Potassium nitrite.}}{KNO_2} + \underset{\text{Potassium nitrate.}}{KNO_3} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\text{Sodium carbonate.}}{Na_2CO_3} + \underset{\text{Nitrogen tetroxide.}}{2NO_2} = \underset{\text{Sodium nitrite.}}{NaNO_2} + \underset{\text{Sodium nitrate.}}{NaNO_3} + \underset{\text{Carbon dioxide.}}{CO_2}$$

Nitrogen tetroxide is a poisonous gas; it is not changed when brought in contact with the air.

The remarks made on the formula of nitric oxide apply also to nitric peroxide. Its specific gravity, however, varies with the temperature. Thus, just above its boiling-point (22°), the specific gravity is 38·3; at 140° it is 23; so that both molecules, NO_2 and N_2O_4, seem to exist.

NITROGEN PENTOXIDE.

Ab

H_2O

2

HNO

Formula, N_2O_5; *molecular weight*, 108; *melts*, 30°; *boils*, 45°.

Also known as *nitric anhydride*.

Mode of preparation.—Nitrogen pentoxide, or nitric anhydride, is prepared by passing a stream of chlorine gas over solid nitrate of silver contained in a glass tube and gently heated, when the chlorine unites with the silver to form silver chloride, and the vapour of nitric anhydride and oxygen are evolved, the nitric anhydride condensing as a white crystalline solid in the cool part of the tube, and the oxygen escaping.

$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5$

$$\underset{\text{Silver nitrate.}}{4AgNO_3} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Silver chloride.}}{4AgCl} + \underset{\text{Nitrogen pentoxide.}}{2N_2O_5} + \underset{\text{Oxygen.}}{O_2}$$

If too much heat is employed, the nitric anhydride is decomposed with explosive force.

Properties. — Nitrogen pentoxide, or nitric anhydride, is the only solid oxide of nitrogen; it is a white crystalline substance. When placed in water it forms nitric acid.

$$\underset{\text{Nitrogen pentoxide.}}{N_2O_5} + \underset{\text{Water.}}{H_2O} = \underset{\text{Nitric acid.}}{2HNO_3}$$

It decomposes spontaneously at ordinary temperatures.

All the oxides of nitrogen are decomposed when they are passed over red hot copper. By this reaction, if the copper be weighed and the nitrogen collected, their composition can be determined.

NITRIC ACID.

NO_3

Formula, HNO_3; *molecular weight*, 63; *commences to boil at* 86°.

Mode of preparation.—Nitric acid is prepared by the distillation of sulphuric acid with any nitrate. One of the natural nitrates, potassium nitrate or sodium nitrate, is employed, and according to the amount of sulphuric acid and the heat used, an acid sulphate or a neutral sulphate of the alkali metal will be left behind in the retort. Thus, if the sulphuric acid be in excess, an acid sulphate is formed:

$$\underset{\text{Potassium nitrate.}}{KNO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Potassium acid sulphate.}}{KHSO_4} + \underset{\text{Nitric acid.}}{HNO_3}$$

by $KNO_3 + KHSO_4 = K_2SO_4 + HNO_3$

the Sulphate, being 1. acid
2 neutral

At a higher temperature, if the nitrate be in excess, a neutral sulphate is formed :

$$\underset{\substack{\text{Potassium}\\\text{nitrate.}}}{2KNO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3}$$

Properties.—Nitric acid, if pure, is a colourless liquid, fuming on exposure to the air, and possessing an irritating smell. Commercial nitric acid consists 70 of 70 per cent. of nitric acid, the remaining ·30 per cent. being water, and it is of specific gravity 1·42. Pure nitric acid is of specific gravity 1·52, and is a somewhat unstable body. *Aquafortis* is an old name for nitric acid, given to it on account of its property of acting on most of the metals; the only common metals not acted on by nitric acid are gold, platinum, and aluminium. A mixture of two parts of nitric acid to four parts of hydrochloric acid is known as *aqua regia*, on account of its property of dissolving gold, the "king of metals." A commercial article known as *yellow* or *fuming nitric acid*, which contains dissolved nitrogen tetroxide, is made by distilling potassium nitrate and strong sulphuric acid in the proportions to form the neutral potassium sulphate, and using a higher temperature than is employed in the manufacture of the ordinary acid. Nitric acid corrodes and stains the skin and articles of clothing yellow ; the colour is not removed but intensified by the application of solution of ammonia. Strong nitric acid is a powerful corrosive and irritant poison.

Tests.—Nitric acid, whether in the free state or in the form of a nitrate, may be detected by the following tests :—(1) To a cold solution of a nitrate, contained in a test-tube, add its own volume of strong sulphuric acid, *mix* and cool under the tap, incline the tube, and pour gently down its side a solution of ferrous sulphate ; a dark brown colour will then appear at the junction of the two liquids, due to the liberated nitrogen dioxide forming a dark brown compound with the ferrous sulphate. This test, when carefully conducted, is very delicate.

(ii) To a solution of a nitrate add some copper turnings, carefully add strong sulphuric acid, and then apply a gentle heat until a free liberation of gas occurs: this gas, which is nitrogen dioxide, will become of a reddish-brown colour as it mixes with the air in the test-tube.

Nitrates can be estimated by converting them into ammonia by nascent hydrogen. The ammonia is then distilled off and estimated by the Nessler test (*see* Ammonia). The hydrogen can be produced by adding some potassium hydrate and aluminium foil to the solution of the nitrate.

$$\underset{\substack{\text{Potassium}\\\text{nitrate.}}}{KNO_3} + \underset{\text{Hydrogen.}}{8H} = \underset{\text{Ammonia.}}{NH_3} + \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{KHO} + \underset{\text{Water.}}{2H_2O}$$

NITRATES.

Nitrates occurring in nature are produced by the oxidation of organic nitrogenous bodies, the resulting nitric acid becoming neutralised by contact with salts of the alkali or alkaline earth metals. In many, if not in all cases, this oxidation of the nitrogen of organic nitrogenous bodies to nitric acid, is brought about by the influence of a ferment called the "nitrifying ferment," which may exist in the soil or in water. The nitre or saltpetre (KNO_3) formed in the surface soil of various parts of India is produced by the oxidation of organic nitrogenous bodies (especially the excreta of animals and human beings), under the influence of the nitrifying ferment and the tropical heat, in a soil rich in potassium salts. The action of this ferment ceases when exposed to the light.

The small quantities of nitrates (nitrates of calcium and magnesium) that may be present in well-waters or river-waters which have been contaminated with sewage are similarly produced by oxidation of the nitrogenous matters of the sewage, under the influence of the ferment, to nitric acid, and subsequent neutralisation of this acid by the carbonate of calcium or magnesium in the water.

A description of the various nitrates and nitrites will be given with their respective metals.

[illegible]
fr. HNO_3 + Zn.
~~[illegible]~~ distill.
Spontaneous decomp. of urine [illegible] ammon. matter
Of nit. bodies heated with strong caustic al[illegible]

Compounds of Nitrogen with Hydrogen

CHAPTER VI.

AMMONIA—AMMONIUM SALTS.

Ammonia—Preparation and Properties of Ammonia—Tests for Ammonia — Ammonium — Sources of Ammonium Salts—Ammonium Chloride—Ammonium Carbonate — Ammonium Nitrate—Ammonium Bromide—Ammonium Sulphide—Ammonium Acetate—Ammonium Citrate—Ammonium Oxalate —Ammonium Benzoate—Tests for Ammonium Salts.

AMMONIA.

H3

Formula, NH_3 ; *molecular weight*, 17 ;
liquefies at $-40°$.

Modes of preparation.—(i) Ammonia gas is best prepared by heating a mixture of dry ammonium chloride and quicklime (CaO) or slaked lime ($Ca(HO)_2$) :

$$\underset{\text{Ammonium chloride.}}{2NH_4Cl} + \underset{\text{Quicklime.}}{CaO} = \underset{\text{Calcium chloride.}}{CaCl_2} + \underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Water;}}{H_2O}$$

or, $$\underset{\text{Ammonium chloride.}}{2NH_4Cl} + \underset{\text{Slaked lime.}}{Ca(HO)_2} = \underset{\text{Calcium chloride.}}{CaCl_2} + \underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Water.}}{2H_2O}$$

The ammonia gas cannot be collected over water, on account of its extreme solubility, but may be collected over mercury, or by upward displacement (*see* Fig. 14), on account of its being lighter than air.

(ii) Ammonia may also be prepared by heating ammonium chloride, or any other ammonium salt, with caustic potash or caustic soda :

(1) heated with Caustic { Soda pota

$$\underset{\text{Ammonium chloride.}}{NH_4Cl} + \underset{\text{Caustic potash.}}{KHO} = \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Potassium chloride.}}{KCl} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\text{Ammonium chloride.}}{NH_4Cl} + \underset{\text{Caustic soda.}}{NaHO} = \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Sodium chloride.}}{NaCl} + \underset{\text{Water.}}{H_2O}$$

$NaNO_3 + 4H_2 = Na$[illegible] $+ 2H_2O + NH_3$

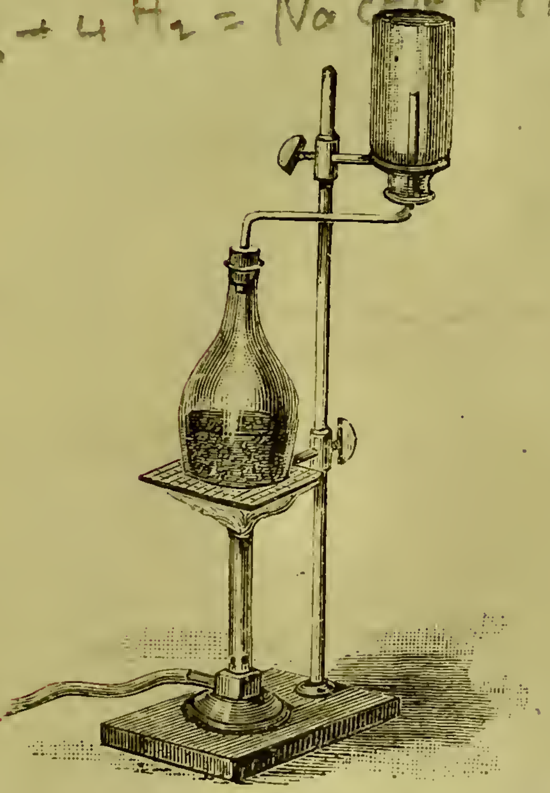


Fig. 14.—Preparation and Collection of Ammonia Gas.

of HNO_3 on other meta

(iii) Ammonia is obtained by the action of dilute nitric acid on the metal zinc:

$$\underset{\text{Zinc.}}{4Zn} + \underset{\text{Nitric acid.}}{9HNO_3} = \underset{\text{Zinc nitrate.}}{4Zn(NO_3)_2} + \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Water.}}{3H_2O}$$

The ammonia is not evolved in this case, but unites with some of the nitric acid to form ammonium nitrate, from which, however, it may be set free by heating with a caustic alkali.

(iv) Ammonia is also obtained by the action of dry heat without contact of air (destructive distillation), on various organic nitrogenous substances of both animal and vegetable origin. Thus, by the destructive distillation of the horns of animals, ammonia may be obtained; hence the derivation of the old name, "spirit of hartshorn," applied to solution of ammonia. Also during the destructive distillation of coal, about half of the nitrogen unites with some of the hydrogen of the coal to form ammonia, which is ultimately found dissolved in the light "tar liquor" floating on the top of the condensed tar.

(v) Ammonia is also formed during the spontaneous decomposition of moist animal matter, and during the putrefaction of urine (*see* Org. Chem. Chap. III.).

(vi) By heating organic nitrogenous bodies with strong caustic alkalies, the nitrogen of the organic bodies is converted into ammonia. Advantage is taken of this fact in determining the proportion of nitrogen present in organic nitrogenous bodies, by ascertaining the amount of ammonia produced, when a weighed quantity of the organic body is heated with a caustic alkali.

Properties.—The specific gravity of ammonia is 8·5, and it is lighter than air; it is a colourless gas, with a characteristic strong pungent odour and alkaline taste; it is feebly combustible, not catching fire in air, but in oxygen it burns with a pale yellowish or greenish-yellow flame; it also burns when mixed with hydrogen or coal gas, forming nitric acid; it is not a supporter of combustion. It is the most soluble of all gases in water; 1 volume of water dissolves over 800 volumes of the gas at ordinary temperatures. It is very easily liquefied by pressure, since at ordinary temperatures under a pressure of seven atmospheres it becomes liquid. It unites readily with acids,

1,050 galls of NH_4 [illegible]
[illegible] H_2O [illegible]

of gas expanded by electric

forming ammonium salts. It must therefore be dried by passing it over quick-lime (CaO). If inhaled in large quantities and in the pure state, it is a poison, on account of its irritating action on the mucous membrane of the respiratory passages. Ammonia is composed of 1 volume of nitrogen united with 3 volumes of hydrogen, the 4 volumes being condensed, as a result of the union, to 2 volumes; therefore, if ammonia gas is decomposed into its elements its volume becomes doubled, thus:

$$\underset{\text{2 molecules.}}{2NH_3} = \underset{\text{1 molecule.}}{N_2} + \underset{\text{3 molecules.}}{3H_2}$$

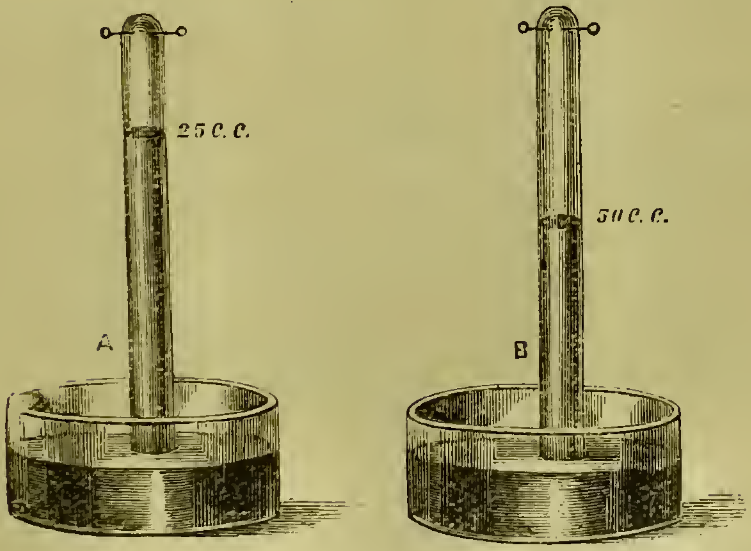


Fig 15.--A, Ammonia gas before the passage of electric sparks; B, after passage of electric sparks for some time (volume doubled).

From which it is seen that 2 molecules of ammonia gas produce 4 molecules of the mixture of nitrogen and hydrogen, and, since the molecules of all gases occupy the same bulk, therefore ammonia gas becomes doubled in bulk when it is resolved into its elements. This decomposition of ammonia gas into its elements can be effected at a high temperature, or by passing electric sparks for some time through the gas confined in a eudiometer over mercury (Fig. 15).

ammonia = really hydrogen [illegible]
[illegible] radicle is NH_2

If after this decomposition into its elements an excess of oxygen be added and the mixture exploded, a great diminution in bulk takes place, owing to the hydrogen uniting with half its volume of oxygen to form a minute drop of water. Two-thirds of this diminution give the hydrogen present in the 25 cc. of ammonia. Thus,

25 cc. of NH_3 on passing sparks = 50 cc. of N + H,
add 30 cc. of oxygen ∴ 80 cc. of N + H + O;
explode, the residual gas measures 23·8 cc.
∴ diminution = 80 — 23·8 = 56·2 cc.;
multiplying by $\frac{2}{3}$ we get 37·5 cc. of H
and (50 - 37·5) 12·5 cc. of N in 25 cc. of NH_3.

Tests.—(i) The odour of the gas constitutes a fairly delicate test.

(ii) Dense white fumes are produced on inserting a rod moistened with strong hydrochloric acid into a jar or tube of the gas.

(iii) Moistened red litmus paper is turned blue when brought in contact with the gas.

(iv) The most delicate test for small quantities of ammonia in solution, as in a drinking-water, is the "Nessler test"; this consists in adding to the water some Nessler reagent (*see* page 258), when a reddish-brown colour or precipitate is produced, according to the amount of ammonia present. This test will detect 1 part of ammonia in 500,000 of water. Up to a certain strength, the *intensity* of the colour produced indicates the *quantity* of ammonia present.

AMMONIUM AND ITS SALTS.

The radicle ammonium (NH_4) has never been isolated, nor has the molecule $(NH_4)_2$. The latter, however, has been obtained in the form of an amalgam

$HCl + NaHg = NH_4Hg + NaCl$

with mercury, by placing sodium amalgam in a strong solution of ammonium chloride, when the ammonium takes the place of the sodium, and a light, bulky amalgam with a metallic lustre is obtained.

This ammonium amalgam is, however, very unstable, and in the course of a few minutes is resolved into free mercury, with escape of ammonia and hydrogen gases.

According to some observers, this amalgam is simply a mass of mercury swollen out by bubbles of ammonia gas.

Sources of the ammonium salts.—(i) The ammonium salts of commerce are principally prepared directly or indirectly from the *ammoniacal tar liquor* of the gasworks (*see* Org. Chem. Chap. V.); this contains, in solution, free ammonia, and on distillation, neutralisation with hydrochloric acid and subsequent concentration of the liquid by evaporation, crystals of ammonium chloride are obtained. (ii) The boracic acid of volcanic origin obtained in Tuscany (*see* page 169) is accompanied by ammonium salts, and on submitting the crude boracic acid to heat with carbonate of soda, a very pure carbonate of ammonium (the so-called volcanic carbonate of ammonium) volatilises and condenses. (iii) As mentioned on page 120, solution of ammonia (spirit of hartshorn) was formerly prepared by the destructive distillation of the horns of animals. (iv) The excreta of some animals, such as camels and serpents, contain large quantities of ammonium salts; and by heating the excreta with sodium chloride (common salt), ammonium chloride volatilises and can be condensed in the solid form.

AMMONIUM SALTS.

Ammonium chloride (NH_4Cl). Also known as *sal ammoniac*. As previously described, this is obtained from the ammoniacal coal-tar liquor of the gasworks.

Ammonium carbonate ($N_4H_{16}C_3O_8$).—Prepared by heating a mixture of solid ammonium chloride and chalk (calcium carbonate), when the ammonium carbonate sublimes as a white solid. This, the commercial ammonium carbonate, is not the normal carbonate, but consists of a mixture of two molecules of the bicarbonate of ammonium (NH_4HCO_3) with one molecule of the carbamate of ammonium ($NH_4NH_2CO_2$), thus:

$$2NH_4HCO_3, NH_4NH_2CO_2 = N_4H_{16}C_3O_8.$$

By dissolving this commercial carbonate in water, the carbamate unites with the elements of water to form the normal carbonate, thus:

$$\underset{\text{Ammonium carbamate.}}{NH_4NH_2CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Normal ammonium carbonate.}}{(NH_4)_2CO_3}$$

Then, if some solution of ammonia be added to this solution, the bicarbonate is also converted into the normal carbonate, thus:

$$\underset{\text{Ammonium bicarbonate.}}{2NH_4HCO_3} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Normal ammonium carbonate.}}{2(NH_4)_2CO_3}$$

So that to prepare a solution of the normal ammonium carbonate, such as is employed as a test-reagent, it is necessary to dissolve the commercial carbonate in water, and then to add some solution of ammonia.

Ammonium nitrate (NH_4NO_3).—Prepared by neutralising nitric acid with ammonium carbonate, or with solution of ammonia.

Ammonium bromide (NH_4Br).—Prepared by neutralising hydrobromic acid with ammonium carbonate, or with solution of ammonia.

Ammonium sulphide ($(NH_4)_2S$).—Prepared by saturating solution of ammonia with sulphuretted hydrogen gas.

$$\underset{\text{Ammonia.}}{2NH_3} \quad + \quad \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{H_2S} \quad = \quad \underset{\substack{\text{Ammonium}\\\text{sulphide.}}}{(NH_4)_2S}$$

Ammonium acetate ($NH_4C_2H_3O_2$), **Ammonium citrate** ($(NH_4)_3C_6H_5O_7$), **ammonium oxalate** ($(NH_4)_2C_2O_4$), and **ammonium benzoate** ($NH_4C_7H_5O_2$) are made by neutralising the respective acids with ammonium carbonate, or with solution of ammonia.

Tests for Ammonium Salts.

(i) If a solution of an ammonium salt be heated
with caustic potash or caustic soda, ammonia gas will
be evolved, which can be recognised by its odour, by 1
its turning moistened red litmus paper blue, and by 2
the white fumes produced when a glass rod moistened 3
with strong hydrochloric acid is brought near it.

(ii) If to a solution of an ammonium salt some Nessler reagent be added, a reddish-brown colour or precipitate will be produced. This reaction is only used for detecting very minute quantities of ammonia.

Other compounds of nitrogen and hydrogen exist, but they are somewhat unstable.

Hydroxylamine (NH_2HO) can be obtained in solution by the action of nascent hydrogen on nitric acid. It has been prepared in the pure state, when it forms a colourless, odourless, crystalline solid, which explodes when heated; it is a powerful reducing substance.

Hydrazine (N_2H_4).—This is a liquid solidifying at $-1°$; it has a dreadful odour, and fumes violently in the air.

Hydrazine hydrate ($N_2H_4H_2O$) is a colourless fuming liquid which attacks and corrodes glass, cork, india-rubber, etc. It is a reducing substance, and forms salts with acids (N_2H_4HCl).

Azoimide (N_3H) is a liquid boiling at 37°, has a fearful odour, is very soluble in water, forming an acid solution resembling hydrochloric acid: thus, it dissolves iron and magnesium, evolving hydrogen, gives a white precipitate with silver nitrate, and forms dense white fumes with ammonia. It explodes with great violence when heated.

① [illegible]
② metallic chl, H_2SO_4 & MnO_2
③ Pass HCl & air over red hot bricks
④ Deacon's Process
⑤ Electrolysis of KCl

CHAPTER VII.

CHLORINE—OXIDES AND ACIDS OF CHLORINE.

Halogen Elements—Chlorine—Preparation and Properties of Chlorine—Tests for Chlorine—Hydrochloric Acid—Nitro-hydrochloric Acid—Chlorine Monoxide or Hypochlorous Anhydride—Chlorine Tetroxide or Chlorine Peroxide—Hypochlorous Acid—Chlorinated Bodies—Chloric Acid—Perchloric Acid.

HALOGEN ELEMENTS.

The halogen elements, viz. fluorine, chlorine, bromine, and iodine, are four elements that are closely allied to one another in their properties. With metals they all form compounds analogous to sea-salt, hence the derivation of the term halogen (from ἅλς, *sea-salt; γεννάω, I produce*). None of them occur free in nature.

CHLORINE.

Symbol, Cl; *molecule*, Cl_2; *monad; atomic weight*, 35·5; *molecular weight*, 71; *liquefies* – 34°.

Chlorine occurs in nature combined with metals as chlorides, of which the commonest is sodium chloride, *sea-salt* or *rock-salt*. The name chlorine is derived from χλωρός, *green*, on account of the greenish-yellow colour of the gas.

HCl

Modes of preparation.—(i) Chlorine is most readily prepared by heating a mixture of strong hydrochloric acid and manganese dioxide (black oxide of manganese), and collecting the gas by downward displacement of air (Fig. 16).

$$\underset{\text{Manganese dioxide.}}{MnO_2} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Manganese chloride.}}{MnCl_2} + \underset{\text{Water.}}{2H_2O} + Cl_2$$

(ii) Chlorine may also be prepared by heating a mixture of common salt, manganese dioxide, and sulphuric acid.

Ow.

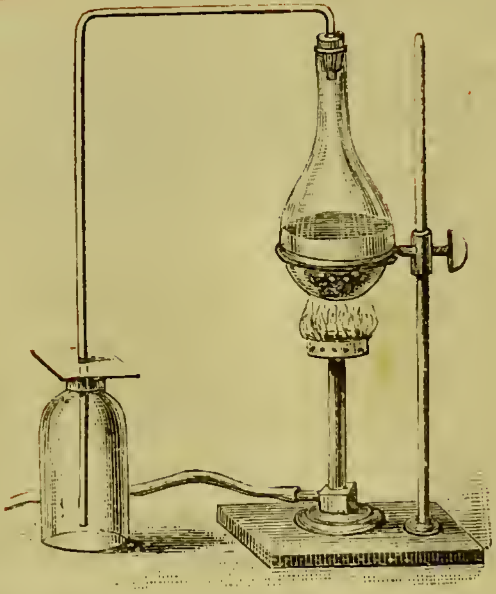


Fig. 16.—Preparation and Collection of Chlorine.

$$\underset{\text{Sodium chloride.}}{2NaCl} + \underset{\text{Manganese dioxide.}}{MnO_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Manganese sulphate.}}{MnSO_4} + \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Chlorine}}{Cl_2} + \underset{\text{Water.}}{2H_2O}$$

In a similar way, chlorine may be obtained by the action of manganese dioxide and sulphuric acid on any metallic chloride.

(iii) By passing a mixture of hydrochloric acid gas and air over red-hot bricks, chlorine is liberated; by this method the chlorine obtained is necessarily mixed with the nitrogen of the air, an admixture of but little importance when the chlorine is to be used for manufacturing purposes.

icks

$$\underset{\text{Hydrochloric acid gas.}}{4HCl} + \underset{\text{Oxygen of the air.}}{O_2} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{2Cl_2}$$

Deacon

(iv) Deacon's process for the manufacture of chlorine consists in passing a mixture of hydrochloric acid gas and air over heated fragments of pumice stone saturated with cupric chloride. The cupric chloride is decomposed into cuprous chloride, evolving one-half of its chlorine.

$$\underset{\text{Cupric chloride.}}{2CuCl_2} = \underset{\text{Cuprous chloride.}}{Cu_2Cl_2} + \underset{\text{Chlorine.}}{Cl_2}$$

The cuprous chloride is then reconverted into cupric chloride by means of chlorine, which is liberated from the hydrochloric acid gas by the oxygen of the air.

$$\underset{\text{Cuprous chloride.}}{2Cu_2Cl_2} + \underset{\text{Hydrochloric acid gas.}}{4HCl} + \underset{\text{Oxygen of the air.}}{O_2} = \underset{\text{Cupric chloride.}}{4CuCl_2} + \underset{\text{Water.}}{2H_2O}$$

The cupric chloride then again becomes reduced to cuprous chloride with evolution of half its chlorine, and so on.

(v) Chlorine may be obtained by the electrolysis of hydrochloric acid, or of a solution of salt, using electrodes of gas-carbon; equal volumes of chlorine and hydrogen are evolved, the chlorine being set free at the positive pole, and the hydrogen or sodium (immediately converted by the water into sodium hydrate and hydrogen) at the negative pole.

Properties.—The specific gravity of chlorine is 35·5; it is a heavy gas, being $2\frac{1}{2}$ times heavier than air. It has a greenish-yellow colour, a very unpleasant suffocating odour, and a disagreeable taste. It is non-combustible, as chlorine will not combine directly with oxygen, but, in an atmosphere of hydrogen, chlorine will burn with a pale livid flame, producing hydrochloric acid; and conversely, hydrogen will burn in an atmosphere of chlorine. Chlorine is a supporter of combustion in a limited sense only; if a burning body contains hydrogen, then it will continue to burn in chlorine with a feeble flame, the chlorine uniting with the hydrogen to form hydrochloric acid, but not uniting with the carbon of the burning body. Thus, if a lighted candle be lowered into a jar of chlorine, the candle will continue to burn with a reddish flame, and all the carbon will be set free as a dense smoke. A piece of glowing charcoal will not burn in chlorine, since it contains no hydrogen. If a piece of paper saturated with oil of turpentine ($C_{10}H_{16}$) be thrown into a jar of chlorine, the turpentine catches fire from the heat produced by the rapid union of the chlorine with the hydrogen, but all the carbon is set free as dense smoke.

Chlorine is also a supporter of combustion as regards the following bodies. A piece of phosphorus catches fire when introduced into chlorine, forming the pentachloride of phosphorus (PCl_5). Chlorine will also combine with all metals, forming metallic chlorides; and if some metals in a fine state of division (such as powdered antimony) be thrown into a jar of chlorine they will ignite spontaneously, from the heat produced by the intensity of the union of the chlorine with the metal. Chlorine is soluble in water, 1 volume of water dissolving about $2\frac{1}{2}$ volumes of the gas; it must, therefore, be collected over hot water, or by displacement, not over mercury, since it would combine with that metal. When submitted to a pressure of six atmospheres, at ordinary temperatures, it is condensed to a yellow liquid.

Chlorine is a poisonous gas, acting as a powerful irritant to the mucous membrane of the respiratory passages. Chlorine is also an important bleaching and

Bleaches only vegetable colours.

disinfecting agent; it bleaches all vegetable colours in presence of moisture, acting in two ways: partly by uniting with the hydrogen of the dye and replacing it by chlorine, and so forming a colourless substitution product; and partly by uniting with the hydrogen of the water and liberating oxygen, which in the nascent state oxidises and destroys the colouring matter. Chlorine does not bleach mineral colours. As a disinfecting agent, chlorine acts as a powerful germicide, but its unpleasant odour and irritating properties when inhaled prevent its general use as a disinfectant. Chlorine is also a deodoriser, acting by virtue of its affinity for hydrogen, by uniting with the hydrogen of bad-smelling gases and so decomposing them; for instance, if chlorine be brought in contact with sulphuretted hydrogen, hydrochloric acid is formed and sulphur precipitated.

$$\underset{\substack{\text{Sulphuretted}\\ \text{hydrogen.}}}{2H_2S} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\substack{\text{Hydrochloric}\\ \text{acid gas.}}}{4HCl} + \underset{\text{Sulphur.}}{S_2}$$

The two most marked chemical properties of
1. chlorine are: ⓐ its property of combining with
2 hydrogen; ⓑ its property of uniting with metals.
Several instances of both these properties have been given; a further illustration of the first-mentioned one may be given here. So great is the power of chlorine of uniting with hydrogen, that if chlorine water be simply exposed to direct sunlight it is decomposed, the chlorine uniting with the hydrogen of the water and setting free the oxygen.

$$\underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{4HCl} + \underset{\text{Oxygen.}}{O_2}$$

If a mixture of equal volumes of hydrogen and

Iod Starch paper turns blue.

chlorine be exposed to sunlight, the mixture will explode.

1 2 3 **Tests.**—(i) The colour, the odour and the fact that a piece of moistened litmus paper (blue or red) is bleached by the gas, constitute very fair tests for chlorine.

4 (ii) The most delicate test for chlorine is based upon the fact of its liberating iodine from iodide of potassium, the liberated iodine in contact with starch forming a blue compound. If a piece of blotting-paper be dipped in a mixed solution of potassium iodide and starch paste, and then be brought in contact with chlorine, it is turned of a blue colour. (N.B.—This reaction is also produced by ozone, and by nitrogen trioxide and peroxide, *see* page 81.)

Drying- Iod becomes active with

HYDROGEN CHLORIDE.

8·25
26=94 Gr.

Formula, HCl; *molecular weight*, 36·5.

A solution of this gas is known as *muriatic acid*, *hydrochloric acid*, and *spirit of salt*. The latter name is applied to an impure form of the acid, which is of a yellowish colour from contamination with ferric chloride; it also generally contains arsenic as an impurity, derived from the impure sulphuric acid that is used in its manufacture.

Modes of preparation.—(i) Hydrogen chloride is most easily prepared by heating a mixture of sodium chloride (common salt) and sulphuric acid.

$$\underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Hydrogen}\\\text{chloride.}}}{2HCl}$$

The hydrogen chloride is given off as a gas, and after washing it through a small quantity of water, it is conveyed into water contained in a bottle kept cool

② Heat H_2SO_4 with any metallic C

by being surrounded with water (Fig. 17). It readily dissolves in the water, and this solution constitutes the hydrochloric acid of commerce.

[illegible]
[illegible] with hydrogen

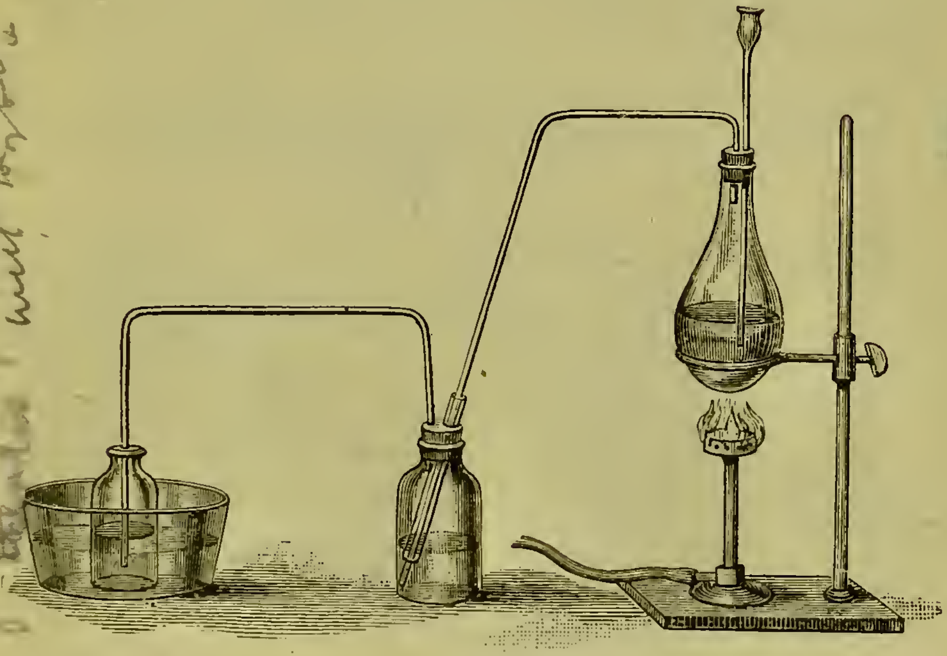


Fig. 17.—Preparation of Hydrochloric Acid.

(ii) In a similar manner, hydrochloric acid may be prepared by heating sulphuric acid with any metallic chloride.

(iii) Hydrogen chloride may be prepared by mixing together equal volumes of hydrogen and chlorine and exposing the mixture of gases to diffused light, when they combine quietly; if the mixture be exposed to strong sunlight, or if a light be applied, the two gases unite suddenly with an explosion. The volume of hydrochloric acid gas formed is exactly equal to the volumes of the constituents; for

$$\underset{\text{1 molecule.}}{H_2} + \underset{\text{1 molecule.}}{Cl_2} = \underset{\text{2 molecules.}}{2HCl}$$

One molecule of hydrogen unites with one molecule of chlorine to produce two molecules of hydrochloric acid gas.

(iv) Hydrogen chloride is also formed when a mixture of steam and chlorine is passed through a red-hot porcelain tube.

p 75

$$\underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{2Cl_2} = \boxed{\underset{\text{Hydrogen chloride.}}{4HCl}} + \boxed{\underset{\text{Oxygen.}}{O_2}}$$

Properties.—Hydrogen chloride is a colourless gas of specific gravity 18·25, and is therefore somewhat heavier than air; it possesses a pungent odour, and an intensely acid taste; it is neither combustible nor a supporter of combustion. It fumes when brought in contact with the air, owing to its dissolving in the moisture of the air, and forming a cloud of hydrochloric acid. It is very soluble in water, 1 volume of water dissolving 454 volumes of the gas at ordinary temperatures; this solution of the gas in water constitutes *hydrochloric* or *muriatic acid.* The acid is a fuming liquid of specific gravity 1·16, and containing 32 per cent. by weight of hydrogen chloride. It is decomposed by a current of electricity (using gas-carbon electrodes) into its elements, equal volumes of chlorine and hydrogen being evolved, the former from the positive pole and the latter from the negative pole (at first only hydrogen is evolved, all the chlorine being dissolved in the fluid).

Hydrochloric acid is very useful in the laboratory as a solvent; it dissolves many metals and oxides forming chlorides: all chlorides are soluble in water except silver, mercurous, cuprous, and lead chlorides (the latter dissolves in hot water).

Tests.—(1) *For the gas.*—It fumes when brought in contact with the air, and also produces a dense white cloud when brought in contact with ammonia gas; it turns blue litmus paper red.

(ii) *For the liquid.*—Nitrate of silver gives a white curdy precipitate, which is insoluble in strong nitric acid, but is soluble in solution of ammonia.

(iii) When hydrochloric acid is heated with MnO_2, chlorine gas is evolved.

NITRO-HYDROCHLORIC ACID OR AQUA REGIA.

This name is given to a mixture of strong nitric and hydrochloric acids; the mixture has a very powerful solvent action on metals. As we have seen, the name *aqua regia* is derived from the fact that it dissolves gold—the "king of metals." Its solvent action on metals is due to the nitric acid, in presence of the metal, liberating chlorine from the hydrochloric acid, the nascent chlorine then uniting with the metal. This is best represented in two equations, thus:

$$\underset{\text{Nitric acid.}}{2HNO_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Water.}}{4H_2O} + \underset{\text{Nitrogen dioxide.}}{2NO} + \underset{\text{Chlorine}}{3Cl_2};$$

then

$$\underset{\text{Gold.}}{2Au} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Gold chloride.}}{2AuCl_3}$$

Oxides of Chlorine

COMPOUNDS OF CHLORINE AND OXYGEN.

Chlorine and oxygen do not unite directly; but indirectly they may be made to form the two following oxides of chlorine:

Cl_2O Chlorine monoxide or hypochlorous anhydride.
Cl_2O_4 Chlorine tetroxide or chlorine peroxide.

CHLORINE MONOXIDE OR HYPOCHLOROUS ANHYDRIDE.

Formula, Cl_2O ; *molecular weight*, 87.

Mode of preparation.—By the action of chlorine gas on the yellow or precipitated mercuric oxide.

$$\underset{\text{Mercuric oxide.}}{2HgO} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Mercuric Oxychloride.}}{Hg_2OCl_2} + \underset{\text{Chlorine monoxide.}}{Cl_2O}$$

Properties.—Chlorine monoxide is a yellowish gas possessing an odour similar to that of chlorine; when heated it decomposes into its elements with explosive violence. It unites with water, forming hypochlorous acid.

$$\underset{\text{Hypochlorous anhydride.}}{Cl_2O} + \underset{\text{Water.}}{H_2O} = \underset{\text{Hypochlorous acid.}}{2HClO}$$

CHLORINE TETROXIDE OR CHLORINE PEROXIDE.

Formula, Cl_2O_4 ; *molecular weight*, 135.

Mode of preparation.—By very gently heating potassium chlorate with pure sulphuric acid, chloric acid is first formed and then breaks up.

$$\underset{\text{Chloric acid.}}{3HClO_3} = \underset{\text{Perchloric acid.}}{HClO_4} + \underset{\text{Chlorine Peroxide.}}{Cl_2O_4} + \underset{\text{Water.}}{H_2O}$$

Properties.—Chlorine tetroxide is a dark yellow gas, exploding with terrific violence when heated. Great care is required in its preparation.

OXYACIDS OF CHLORINE.

There are three oxyacids of chlorine, viz.:

$HClO$	Hypochlorous acid.
$HClO_3$	Chloric "
$HClO_4$	Perchloric "

HYPOCHLOROUS ACID.

Formula, $HClO$.

Mode of preparation.—(i) By the action of hypochlorous anhydride on water.

$$\underset{\text{Hypochlorous anhydride.}}{Cl_2O} + \underset{\text{Water.}}{H_2O} = \underset{\text{Hypochlorous acid.}}{2HClO}$$

(ii) By shaking chlorine water with calcium carbonate.

$$\underset{\text{Calcium carbonate}}{CaCO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Hypochlorous acid.}}{2HClO} + \underset{\text{Calcium chloride.}}{CaCl_2}$$

Properties and compounds.—Hypochlorous acid when mixed with hydrochloric acid suffers decomposition, chlorine being evolved.

$$\underset{\text{Hypochlorous acid.}}{HClO} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Chlorine.}}{Cl_2} + \underset{\text{Water.}}{H_2O}$$

Hypochlorous acid enters into the composition of the **chlorinated bodies**, which consist of a mixture of a chloride and a hypochlorite. The following are the principal chlorinated bodies:—

hlorinated bodies prep

$CaCl_2, Ca(ClO)_2$	Chlorinated	lime.
$NaCl, NaClO$	,,	soda.
$KCl, KClO$	,,	potash.

They are made by the action of chlorine gas on the caustic alkalies, or on the soluble alkaline carbonates. When acted on by acids they evolve their chlorine; when their solutions are boiled they split up into chlorates and chlorides.

Chlorinated lime.—This is prepared by passing chlorine over damp slaked lime.

$$\underset{\text{Slaked lime.}}{2Ca(HO)_2} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Chlorinated lime.}}{CaCl_2, Ca(ClO)_2} + \underset{\text{Water.}}{2H_2O}$$

Properties.—Chlorinated lime constitutes *bleaching powder*, or the disinfectant known as *chloride of lime*. When treated with an acid, such as sulphuric acid, hydrochloric and hypochlorous acids are first set free, and then immediately react on one another, producing free chlorine.

$$\underset{\text{Chlorinated lime.}}{CaCl_2, Ca(ClO)_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Calcium sulphate.}}{2CaSO_4} + \underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Hypochlorous acid;}}{2HClO}$$

then

$$\underset{\text{Hydrochloric acid}}{HCl} + \underset{\text{Hypochlorous acid.}}{HClO} = \underset{\text{Chlorine.}}{Cl_2} + \underset{\text{Water.}}{H_2O}$$

Chlorinated lime is acted on by the weakest acids, for even when exposed to the air, the carbon dioxide (carbonic acid gas) of the air sets free hypochlorous acid, which then decomposes with evolution of chlorine; it is in this way that *chloride of lime* acts as a disinfectant. Its bleaching powers also depend on the evolution of chlorine. If a solution of

{ Na
K.

chlorinated lime be boiled, it yields chlorate and chloride of calcium.

$$\begin{array}{cccccc} 3(\mathrm{CaCl_2, Ca(ClO)_2}) & = & \mathrm{Ca(ClO_3)_2} & + & 5\mathrm{CaCl_2} \\ \text{Chlorinated lime.} & & \text{Calcium chlorate.} & & \text{Calcium chloride.} \end{array}$$

Solid bleaching powder is probably a special compound of calcium, chlorine, and oxygen, having the formula $\left\{ \mathrm{Ca}^{\mathrm{Cl}}_{\mathrm{OCl}} \right.$; since, if it contained calcium chloride, it should be deliquescent, and alcohol ought to dissolve out calcium chloride. Good bleaching powder is not deliquescent, and no $CaCl_2$ is extracted by alcohol. Moreover, if dry bleaching powder be warmed to 70° and carbon dioxide be passed over it, all the chlorine is evolved, and it is improbable that a chloride should be thus decomposed. When bleaching powder is dissolved in water it seems to break up into a mixture of calcium chloride and calcium hypochlorite. The above formula ($CaOCl_2$) was first proposed by Odling.

Chlorinated soda.—Prepared by passing chlorine into solution of caustic soda or solution of sodium carbonate.

$$\begin{array}{cccccccc} 2\mathrm{NaHO} & + & \mathrm{Cl_2} & = & \mathrm{NaCl, NaClO} & + & \mathrm{H_2O} \\ \text{Caustic soda.} & & \text{Chlorine.} & & \text{Chlorinated soda.} & & \text{Water;} \end{array}$$

or

$$\begin{array}{cccccccc} \mathrm{Na_2CO_3} & + & \mathrm{Cl_2} & = & \mathrm{NaCl, NaClO} & + & \mathrm{CO_2} \\ \text{Sodium carbonate.} & & \text{Chlorine.} & & \text{Chlorinated soda.} & & \text{Carbon dioxide.} \end{array}$$

Properties.—The properties of chlorinated soda are similar to those of chlorinated lime. Acids liberate chlorine from it; boiling its solution converts it into chlorate and chloride of sodium.

Chlorinated potash.—Preparation and properties similar to those of chlorinated soda.

CHLORIC ACID.

Formula, $HClO_3$.

Mode of preparation.—Chloric acid is most readily prepared by cautiously adding sulphuric acid to a solution of barium chlorate, allowing the precipitated barium sulphate to subside, and then pouring off the clear liquid.

$$\underset{\text{Barium chlorate.}}{Ba(ClO_3)_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Chloric acid.}}{2HClO_3} + \underset{\text{Barium sulphate.}}{BaSO_4}$$

Properties.—Chloric acid is a most powerful oxidising agent. Its salts are the chlorates, of which the most important is potassium chlorate. No chlorates exist in nature, they therefore have to be made artificially, and, as previously mentioned, they are readily obtained by boiling solutions of the chlorinated bodies.

Potassium chlorate ($KClO_3$).—Prepared by boiling a solution of chlorinated potash (*see* page 139), or by passing chlorine into a heated solution of caustic potash, in which case the chlorinated potash is first formed, and is then immediately decomposed by the heat into potassium chlorate and chloride.

$$\underset{\text{Potassium hydrate.}}{6KHO} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Potassium chlorate.}}{KClO_3} + \underset{\text{Potassium chloride.}}{5KCl} + \underset{\text{Water.}}{3H_2O}$$

On concentrating the solution by evaporation, and then allowing it to cool, the potassium chlorate crystallises out, leaving the more soluble potassium chloride in solution.

Test.—When a chlorate is gently heated with strong sulphuric acid a yellow gas, peroxide of chlorine, is evolved, which detonates when heated (*see* page 136).

PERCHLORIC ACID.

Formula, $HClO_4$.

Mode of preparation.—If potassium chlorate be strongly heated it evolves all its oxygen, leaving potassium chloride; but if it be heated until it just melts, and then kept for a short time at that temperature, only one-third of the oxygen is evolved, and a mixture of potassium perchlorate and chloride is left.

$$\underset{\text{Potassium chlorate.}}{2KClO_3} = \underset{\text{Potassium perchlorate.}}{KClO_4} + \underset{\text{Potassium chloride.}}{KCl} + \underset{\text{Oxygen.}}{O_2}$$

From this mixture the potassium chloride can be removed by virtue of its greater solubility in water, and the perchlorate obtained pure.

By heating potassium perchlorate with sulphuric acid, perchloric acid distils over.

$$\underset{\text{Potassium perchlorate.}}{2KClO_4} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Potassium sulphate.}}{K_2SO_4} + \underset{\text{Perchloric acid.}}{2HClO_4}$$

Properties.—Perchloric acid is a colourless fuming liquid, and is a very powerful oxidising agent. The perchlorates do not evolve an explosive gas when heated with strong sulphuric acid.

bittern (Sea wat
Stassfurt Salt.

ith H_2SO_4 & MnO_2.

CHAPTER VIII.

BROMINE—IODINE—FLUORINE.

Bromine—Preparation and Properties of Bromine—Tests for Bromine—Hydrobromic Acid—Hypobromous Acid—Sodium Hypobromite—Iodine—Preparation and Properties of Iodine—Tests for Iodine—Hydriodic Acid—Iodic Acid—Chlorides of Iodine—Iodide of Nitrogen—Fluorine—Hydrofluoric Acid.

BROMINE.

Symbol, Br; *molecule*, Br_2; *monad; atomic weight*, 80; *molecular weight*, 160. *Boils at* 59°; *freezes at* —7°.

Bromine does not occur in nature in the free state, but in the form of metallic bromides. The bromides of sodium and magnesium are present in small quantities in many mineral springs, and in sea-water; bromide of potassium is also present in the Stassfurt salts, which occur as deposits on a large scale in Northern Germany.

Mode of preparation.—Bromine may be prepared from the mother liquors of mineral spring waters, or from *bittern*, the mother liquor of concentrated sea-water (from which most of the chlorides have crystallised out), or from Stassfurt salts. The bromine is set free by distilling the mother liquors or the Stassfurt salts with sulphuric acid and manganese dioxide, using only sufficient of these two bodies to liberate the bromine, otherwise the chlorine would also be liberated from the chlorides that are always present, and would contaminate the bromine by forming with it a chloride of bromine. The liberation of the bromine, by the manganese dioxide and sulphuric acid, takes place in a similar manner to the liberation of chlorine by the same reagents.

$$\underset{\text{Sodium bromide.}}{\mathrm{2NaBr}} + \underset{\text{Manganese dioxide.}}{\mathrm{MnO_2}} + \underset{\text{Sulphuric acid.}}{\mathrm{2H_2SO_4}} = \underset{\text{Bromine.}}{\mathrm{Br_2}} + \underset{\text{Sodium sulphate.}}{\mathrm{Na_2SO_4}} + \underset{\text{Manganese sulphate.}}{\mathrm{MnSO_4}} + \underset{\text{Water.}}{\mathrm{2H_2O}}$$

The bromine passes over as a heavy reddish-brown vapour, which is condensed to a liquid by means of a suitable condenser and cool receiver. The bromine so obtained generally contains small quantities of chlorine, present as chloride of bromine, from which it can be purified by redistilling with some potassium bromide, thus :—

$$\underset{\text{Bromine chloride.}}{\mathrm{BrCl}} + \underset{\text{Potassium bromide.}}{\mathrm{KBr}} = \underset{\text{Potassium chloride.}}{\mathrm{KCl}} + \underset{\text{Bromine.}}{\mathrm{Br_2}}$$

Properties.—Bromine is a heavy liquid (bromine and mercury are the only elements liquid at ordinary temperatures) of a dark red-brown colour, and of specific gravity 3·18 at 0°. It is very volatile, forming a reddish-brown vapour possessing a disagreeable odour, somewhat resembling that of chlorine, but much more intense; this vapour is poisonous, and is extremely irritating to the mucous membranes of the eye, nose, and respiratory passages; the name of the element is derived from *βρῶμος, a stink*, on account of its extremely disagreeable smell. It is soluble to a certain extent in water, bromine-water being of a reddish-brown colour. Its chemical affinities for hydrogen and the metals are weaker than those of chlorine, which can be demonstrated by adding a few drops of chlorine-water to a solution of potassium bromide, when the development of a reddish-brown colour in the solution indicates the liberation of the bromine, thus:

$$\underset{\text{Potassium bromide.}}{2KBr} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Potassium chloride.}}{2KCl} + \underset{\text{Bromine.}}{Br_2}$$

Tests.—In the pure state, bromine is readily recognised by its colour and smell; in the diluted state, such as in weak bromine-water, it may be recognised (*a*) by its colour becoming intensified by the addition of some decoction of starch; (*b*) by giving a white precipitate on the addition of an aqueous solution of carbolic acid; (*c*) by shaking with a drop of chloroform or carbon bisulphide, which dissolves out the bromine and becomes coloured brown.

HYDROGEN BROMIDE.

Formula, HBr; *molecular weight*, 81.

Hydrogen bromide, like hydrogen chloride, is a colourless gas, fuming when brought in contact with the air, and very soluble in water, its solution forming the commercial hydrobromic acid.

Modes of preparation.—Hydrogen bromide cannot be prepared by the action of strong sulphuric acid on a bromide, because the acid decomposes the hydrogen bromide, so that free bromine is liberated.

(i) By the action of bromine on phosphorus in the presence of water.

$$\underset{\text{Phosphorus}}{P} + \underset{\text{Bromine}}{5Br} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Hydrogen bromide.}}{5HBr} + \underset{\text{Phosphoric acid.}}{H_3PO_4}$$

(ii) Hydrobromic acid is very easily prepared by shaking together strong solutions of potassium bromide and tartaric acid, the mixture is then allowed to stand for some time to enable the precipitated acid tartrate of potassium to subside, and the clear solution of hydrogen bromide can then be poured off from the precipitate.

$$\underset{\text{Potassium bromide.}}{KBr} + \underset{\text{Tartaric acid.}}{H_2C_4H_4O_6} = \underset{\text{Hydrobromic acid.}}{HBr} + \underset{\text{Potassium acid tartrate.}}{KHC_4H_4O_6}$$

(iii) Hydrogen bromide is obtained by distilling potassium bromide with phosphoric acid, phosphate of potassium being formed, and hydrobromic acid passing over.

(iv) By passing sulphuretted hydrogen through bromine-water, a solution of hydrogen bromide is formed and sulphur precipitated.

$$\underset{\text{Bromine.}}{2Br_2} + \underset{\text{Sulphuretted hydrogen.}}{2H_2S} = \underset{\text{Hydrobromic acid.}}{4HBr} + \underset{\text{Sulphur.}}{S_2}$$

(v) Hydrogen and bromine may be made to unite by heat.

$$\underset{\text{Hydrogen.}}{H_2} + \underset{\text{Bromine.}}{Br_2} = \underset{\text{Hydrogen bromide.}}{2HBr}$$

Tests.—(i) On the addition of a few drops of chlorine-water to a solution of hydrobromic acid or a bromide, bromine is liberated, a yellowish-red colour being communicated to the solution; on shaking with a drop of chloroform or carbon disulphide the bromine is dissolved and colours the drop brown.

(ii) On the addition of nitrate of silver to a solution of hydrobromic acid or a bromide, a whitish precipitate is formed, insoluble in nitric acid, and but sparingly soluble in ammonia.

OXYACIDS OF BROMINE.

There are two of these acids, viz. :

$HBrO$ Hypobromous acid.
$HBrO_3$ Bromic ,,

HYPOBROMOUS ACID.

Formula, $HBrO$.

Prepared by shaking bromine-water with the yellow precipitated mercuric oxide.

$$\underset{\text{Mercuric oxide.}}{2HgO} + \underset{\text{Bromine.}}{2Br_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Mercuric oxybromide.}}{Hg_2OBr_2} + \underset{\text{Hypobromous acid}}{2HBrO}$$

Sodium hypobromite ($NaBrO$), formed by shaking bromine with cold solution of sodium hydrate, is employed in the estimation of urea in urine. It decomposes the urea, oxidising the carbon and hydrogen to carbon dioxide and water, and setting free the nitrogen, thus :

$$\underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\text{Sodium hypobromite.}}{3NaBrO} = \underset{\text{Sodium bromide.}}{3NaBr} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Nitrogen.}}{N_2}$$

The nitrogen can then be collected and measured (the process is described fully in Organic Chemistry, Chapter III.).

IODINE.

Symbol, I ; *molecule*, I_2 ; *monad ; atomic weight*, ~~127 ;~~ 126·5 *molecular weight*, 254 ; *melts at* 107° ; *boils at* 175°.

Iodine does not occur in nature in the free state. The iodides of sodium and magnesium are present in small quantities in certain mineral spring waters, and in still smaller quantities in sea-water. Large quantities of iodine are now obtained from the deposits of "nitrates" in Chili, where it occurs as sodium iodate. The amount of iodides (mainly sodium iodide) present in sea-water is so minute as to make it impracticable to extract the iodine from sea-water, but sea-weeds possess the property of absorbing the iodides into their tissues in considerable quantities, and it is from sea-weeds that iodine is extracted. The sea-weeds (Scottish and Irish sea-weeds being especially rich in iodine) are collected, dried, and burnt, when an ash named *kelp* is obtained, and it is from this kelp that iodine is prepared. The bulk of the kelp, or sea-weed ash, consists of sodium carbonate, together with sodium chloride, sodium sulphate and sodium sulphide, and small quantities of sodium and magnesium iodides.

Mode of preparation of iodine from kelp.—(i) The kelp is treated with boiling water, and the solution poured off from insoluble matter; (ii) to the solution sulphuric acid is added, when carbon dioxide and sulphuretted hydrogen gases are evolved, sulphur is thrown down, and after standing for twenty-four hours a large quantity of sodium sulphate crystallises out; (iii) the mother liquor from the sodium sulphate crystals is then poured off, and contains in solution the iodides with some sodium chloride and free sulphuric acid; to it manganese dioxide is added, and the mixture distilled at a temperature not exceeding 80°, at which temperature the manganese dioxide and sulphuric acid liberate the iodine, but not the chlorine, or only in very small quantities.

The iodine passes over in the form of a violet-coloured vapour, which is made to pass through a series of cooled glass condensers, on the sides of

$$\underset{\substack{\text{Sodium}\\\text{iodide.}}}{2NaI} + \underset{\substack{\text{Manganese}\\\text{dioxide.}}}{MnO_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Manganese}\\\text{sulphate.}}}{MnSo_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Iodine.}}{I_2}$$

which it condenses as a dark-coloured solid. The iodine so prepared generally contains a small quantity of chlorine in the form of a chloride of iodine, from which it can be purified by resubliming it from some potassium iodide.

$$\underset{\substack{\text{Iodine}\\\text{chloride.}}}{ICl} + \underset{\substack{\text{Potassium}\\\text{iodide.}}}{KI} = \underset{\substack{\text{Potassium}\\\text{chloride.}}}{KCl} + \underset{\text{Iodine.}}{I_2}$$

Preparation from Chili saltpetre.—After the bulk of the sodium nitrate has crystallised out, the mother liquor contains about 22 per cent. of sodium iodate; it is treated with a mixture of sodium sulphite and bisulphite, when the iodine is precipitated as a black deposit, which is ladled out, squeezed, and sublimed.

$$\underset{\substack{\text{Sodium}\\\text{iodate.}}}{2NaIO_3} + \underset{\substack{\text{Sodium}\\\text{sulphite.}}}{3Na_2SO_3} + \underset{\substack{\text{Sodium}\\\text{bisulphite.}}}{2HNaSO_3} = \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{5Na_2SO_4} + \underset{\text{Iodine.}}{I_2} + \underset{\text{Water.}}{H_2O}$$

Properties.—Iodine is a solid crystalline substance, possessing a dark grey colour, a metallic lustre, and a peculiar odour somewhat resembling that of diluted chlorine. When heated it volatilises, producing a violet-coloured vapour (hence its name, from *ἰώδης, violet-coloured*), which is very irritating to the mucous membrane of the eyes and nose. Iodine possesses a strong unpleasant taste, it stains the skin yellow, and is poisonous. It is slightly soluble in water, to which it imparts a yellowish-brown colour; it is much more soluble in a solution of iodide of potassium, in alcohol, ether, chloroform, and bisulphide of carbon.

Tests.—(i) A solution of free iodine gives with a cold decoction of starch a deep blue colour.

(ii) If with an aqueous solution of iodine some chloroform or bisulphide of carbon be well agitated, and the mixture allowed to stand, the chloroform or bisulphide of carbon will settle to the bottom of the tube, carrying the iodine in solution, a pink or purple colour being imparted to the chloroform or bisulphide of carbon by the dissolved iodine.

HYDROGEN IODIDE.

Formula, HI; *molecular weight*, 128.

Hydrogen iodide, like hydrogen chloride and hydrogen bromide, is a colourless gas, fuming when brought in contact with the air, and very soluble in water, its solution forming the ordinary hydriodic acid.

Hydrogen iodide can be prepared by union of its elements, but only with great difficulty. By distilling potassium iodide with strong sulphuric acid, hydrogen iodide is formed, but is immediately decomposed by the acid, iodine being set free.

Modes of preparation.—These are exactly analogous to the methods used to prepare hydrogen bromide.

The equations on p. 144 give the reactions, if iodine be substituted for bromine.

Properties.—Both chlorine and bromine have stronger affinities for hydrogen and for the metals than iodine, therefore both chlorine and bromine possess the property of liberating iodine from hydriodic acid or from an iodide, thus:

$2HI$	+	Cl_2	=	$2HCl$	+	I_2
Hydriodic acid.		Chlorine.		Hydrochloric acid.		Iodine.

$2HI$	+	Br_2	=	$2HBr$	+	I_2
Hydriodic acid.		Bromine.		Hydrobromic acid.		Iodine

Hydriodic acid on exposure to light becomes coloured from liberation of iodine.

Tests.—(i) On the addition of a few drops of chlorine-water to a solution of hydriodic acid or of an iodide, a yellowish-brown colour is produced, due to the liberation of iodine; if some solution of starch be added to this, a deep blue colour will be produced.

(ii) On the addition of nitrate of silver to a solution of hydriodic acid or of an iodide, a yellowish precipitate is formed, insoluble in nitric acid, and almost insoluble in ammonia.

IODIC ACID.

Formula, HIO_3.

Iodic acid is a white crystalline substance, and is prepared (i) by the action of strong nitric acid on iodine, (ii) by passing chlorine into iodine-water.

I_2	+	$6H_2O$	+	$5Cl_2$	=	$2HIO_3$	+	$10HCl$
Iodine.		Water.		Chlorine.		Iodic acid.		Hydrochloric acid.

CHLORIDES OF IODINE.

There are two compounds of iodine and chlorine, viz. ICl, a liquid, and ICl_3, a solid. They are both obtained by direct union of the elements.

IODIDE OF NITROGEN.

This is obtained by mixing a strong alcoholic solution of iodine (such as tincture of iodine) with an aqueous solution of ammonia; various formulæ have been assigned to this substance, NI_3, NH_3I_2, etc.; the latest is $N_2H_3I_3$.

Properties.—Iodide of nitrogen is a dark-coloured powder, which when dried explodes violently with the slightest touch, decomposing into its elements. The importance to medical men of bearing in mind its existence lies in the fact that free iodine and ammonia are incompatibles, and should not therefore be prescribed together in a liniment.

FLUORINE.

Symbol, F; *molecule*, F_2; *monad; atomic weight*, 19; *molecular weight*, 38.

Fluorine occurs in nature as *fluor-spar* or calcium fluoride (CaF_2), and as *cryolite*, a double fluoride of aluminium and sodium (AlF_3, $3NaF$) found in Greenland. The fluorides of calcium and sodium are also present in minute quantities in the blood, bones, and teeth of human beings and animals.

Fluorine was first satisfactorily isolated by Moissan in 1886. This chemist obtained it by the electrolysis of a solution of potassium fluoride in hydrofluoric acid, using a platinum U-tube, and keeping the solution at a temperature of −23°. It is a pale yellowish-green gas, liquefied by Dewar and Moissan at a temperature of −187°. It combines, usually with great violence, with all elements except oxygen, nitrogen, and chlorine.

HYDROGEN FLUORIDE.

Formula, HF.

Like the corresponding compounds with chlorine, bromine, and iodine, hydrogen fluoride is a colourless gas, fuming on contact with the air, and very soluble in water, its solution constituting the commercial hydrofluoric or fluoric acid.

Mode of preparation.—Hydrogen fluoride is obtained by the action of strong sulphuric acid on powdered fluor-spar, thus :

$$\underset{\substack{\text{Calcium}\\\text{fluoride,}}}{CaF_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Hydrogen}\\\text{fluoride.}}}{2HF} + \underset{\substack{\text{Calcium}\\\text{sulphate.}}}{CaSO_4}$$

It has to be prepared in leaden or platinum vessels, as it readily attacks glass ; on conducting the gas into water, the commercial solution of hydrofluoric acid is obtained.

Properties.—The most important property of this acid is its power of etching glass, which is due to its attacking the silica of glass, forming with it a gaseous silicon fluoride, thus :

$$\underset{\text{Silica.}}{SiO_2} + \underset{\substack{\text{Hydrofluoric}\\\text{acid.}}}{4HF} = \underset{\substack{\text{Silicon}\\\text{fluoride.}}}{SiF_4} + \underset{\text{Water.}}{2H_2O.}$$

If a design is to be etched on glass, the surface of the glass is first covered with wax, the design is then scratched through the wax, and the surface exposed for a few minutes to the fumes of hydrofluoric acid (evolved from fluor-spar and sulphuric acid), or the solution of hydrofluoric acid is poured over the surface ; on washing the surface with a stream of water, and then scraping or melting off the wax, the design will be found to be etched on the glass. On account of its power of attacking glass, the solution of hydrofluoric acid is kept in bottles made of gutta-percha, provided with a stopper of the same material.

Test.—The test for hydrofluoric acid is to expose to it a piece of waxed glass, on which some simple design has been scratched, when the design will in a short time be etched on the glass.

CHAPTER IX.

CARBON—SILICON—BORON.

Carbon—Allotropic forms of Carbon—Properties of Carbon—Carbon Monoxide—Preparation and Properties of Carbon Monoxide—Carbon Dioxide—Preparation and Properties of Carbon Dioxide—Carbon Oxychloride—Carbon Bisulphide—Silicon, Silica, Silicates, Glass, Porcelain, and Earthenware—Boron—Boric Acid—Metaboric Acid—Borax.

CARBON.

Symbol, C; *tetrad; atomic weight* 12.

CARBON occurs in nature in the free state in the diamond, graphite, plumbago, coal, etc. In the combined state it enters into the composition of an immense number of bodies, for the number of carbon compounds (both natural and artificial) far exceeds those of any other element; it occurs in all organic substances, whether of animal or vegetable origin, and in all carbonates, such as marble, limestone, chalk, magnesite, etc.

Carbon exists in three allotropic forms, of which two are crystalline, viz. *diamond* and *graphite*, and one amorphous, viz. *charcoal* in its different forms. The term *allotropic* (from ἄλλος, *another*; τρόπος, *condition*) is applied to elements that are similar in composition, but differ in their properties.

The allotropic forms of carbon.—(1) *Diamond.*—This is the rarest form of free carbon, and occurs in nature in octahedral crystals belonging to the regular system; it consists of nearly pure carbon, but when a diamond is burnt in oxygen, a minute amount of ash is left, consisting of silica, alumina, and sometimes oxide of iron. It is the hardest body known, and is employed for cutting glass; the property of *cutting* glass depends on the *curved* edge which many diamond crystals possess. Its lustre is due to its high power of refracting light. Moissan has prepared microscopic crystals of diamond by dissolving carbon in melted iron and cooling the whole suddenly. The iron is dissolved by acids, and in the residue some minute diamond crystals are found.

(2) *Graphite, plumbago,* or *blacklead.*—This is the second crystalline form of carbon, and crystallises in six-sided plates. It is a dark-grey crystalline substance, soft and greasy to the touch, and when drawn across paper leaves a mark. It is employed in blacklead pencils, in plumbago crucibles (made of plumbago mixed with clay), for blacking iron grates, and as a dry lubricant for machinery.

(3) *Amorphous carbon.*—This occurs in various forms.

(*a*) *Wood charcoal* is prepared by heating or charring wood out of contact with air. This form of amorphous carbon is used in the manufacture of gunpowder. It is extremely porous, possessing the power of absorbing gases, and hence is used as a deodoriser.

(*b*) *Animal charcoal* is obtained by heating bones out of contact with air. This form of amorphous carbon is sold commercially under the names of *bone-black, animal-black,* and *ivory-black;* it contains the inorganic constituents of the bones, viz. phosphate and carbonate of lime, from which, however, it may be freed by digesting with hydrochloric acid, which dissolves these lime salts, so that on filtering, and washing the charcoal with water, it is obtained pure. Animal charcoal possesses in a very high degree the power of absorbing colouring matters, and hence is very useful as a decolorising agent. In the preparation of several of the alkaloids, the colouring matter is removed by boiling the alkaloidal solution with animal charcoal. In the manufacture of sugar, the crude brown syrup is filtered hot through animal charcoal to decolorise it.

(*c*) Amorphous carbon is the chief constituent of *coal*. Coal has been produced by the slow decay of vegetable matter out of contact with air, possibly combined with elevation of temperature and considerable pressure.

(*d*) *Peat*, another form of fuel, but inferior to coal, contains a quantity of amorphous carbon; it is produced in marshy localities by the gradual decay of grasses, mosses, etc.

(*e*) *Tinder* is a variety of amorphous carbon.

(*f*) *Soot* and *lampblack* are two varieties of amorphous carbon in a fine state of division.

Properties of carbon.—In all three of its forms carbon is infusible at all temperatures, but it volatilises at the high temperature of the electric arc. It is insoluble in all ordinary solvents, but molten iron at the temperature of the blast-furnace dissolves from 4 to 5 per cent. of carbon; as the iron cools part of the carbon crystallises out as small crystals of graphite, and part remains in union with the iron as carbide of iron (Metals, Chapter VII., Cast Iron). Carbon when heated to redness has a powerful affinity for oxygen, either in the free state as in air, or in the combined state; it is therefore largely employed as a reducing agent for depriving many of the metallic oxides of their oxygen, and so reducing them to the metallic state. If carbon be burnt in a free supply of air it produces carbon dioxide (CO_2), but if burnt in a limited supply of air it produces mainly carbon monoxide (CO).

Carbon produces with hydrogen a large number of compounds known as hydrocarbons, some of which will be described later; one such compound is obtained by direct union of carbon and hydrogen, viz. *acetylene* (C_2H_2), at the extremely high temperature of the electric arc; if the electric arc is produced between carbon poles in an atmosphere of hydrogen, then the two elements unite to form acetylene, thus:

$$\underset{\text{Carbon.}}{2C} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Acetylene.}}{C_2H_2}$$

Test.—Any form of carbon (including the diamond) when burnt in oxygen produces carbon dioxide, which can be recognised by its turning lime water turbid.

CARBON MONOXIDE.

See p. 174
O.S.S.

Formula, CO; *molecular weight*, 28;
liquefies —190°.

Also known as *carbonic oxide*.

Modes of preparation.—(i) By passing carbon dioxide through a tube containing pieces of red hot charcoal.

15. by reducing CO_2

$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Carbon.}}{C} = \underset{\text{Carbon monoxide.}}{2CO}$$

The blue flames seen at the top of a well-drawing clear fire consist of burning carbon monoxide, which has been produced by the carbon dioxide, formed at the lower part of the fire, having to pass over the red-hot coal on its upward way to the chimney.

(ii) Carbon monoxide is very easily prepared by heating potassium ferrocyanide with strong sulphuric acid.

$$\underset{\text{Potassium ferrocyanide.}}{K_4Fe(CN)_6} + \underset{\text{Sulphuric acid.}}{6H_2SO_4} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Potassium sulphate.}}{2K_2SO_4} +$$

Gives Equal vol. of CO + CO2. $(H_2C_2O_4)$

$$\underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Ammonium sulphate.}}{3(NH_4)_2SO_4} + \underset{\text{Carbon monoxide.}}{6CO}$$

(iii) Carbon monoxide is also readily prepared by heating formic acid ($HCHO_2$) or sodium formate ($NaCHO_2$) with strong sulphuric acid. The action of the sulphuric acid is simply to abstract water from the formic acid, when carbon monoxide is evolved, thus:

$$\underset{\text{Formic acid.}}{HCHO_2} = \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon monoxide.}}{CO}$$

or gently heat a mixture of $NaCHO_2 + H_2SO_4 = NaHSO_4 +$

(iv) If oxalic acid ($H_2C_2O_4$) be heated with strong sulphuric acid, it decomposes into water and the two oxides of carbon, thus: Cf. test for oxalate.

$$\underset{\text{Oxalic acid.}}{H_2C_2O_4} = \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon monoxide.}}{CO} + \underset{\text{Carbon dioxide.}}{CO_2}$$

COOH
COOH

The Excess of H_2SO_4 removes the

By passing the two gases through a strong solution of caustic potash, the carbon dioxide is absorbed (forming potassium carbonate), and the carbon monoxide can then be collected in the pure state.

(v) When charcoal or carbonaceous substances are burnt with an insufficient supply of air, carbon monoxide is formed.

Properties.—The specific gravity of carbon monoxide is 14, and it is slightly lighter than air; it is a colourless, almost odourless, and tasteless gas; it is combustible, burning with a pale blue flame, and forming carbon dioxide; it is a non-supporter of combustion; it is insoluble in water, and therefore may be collected over it. It is a poisonous gas, as it possesses the property of displacing the oxygen from its union with the hæmoglobin of the blood, forming a compound with the hæmoglobin which acts as a narcotic poison; inhaling the fumes of burning charcoal, placed in the

pour a few cc. of NaOH into the jar & shake well. Half the vol. is gone disappears (Na [illegible] is formed) ueH] $CO + CO_2 + H_2O$

alic acid

$COOH = CO + H_2O$.

centre of a closed and non-ventilated room (a not uncommon method of committing suicide in France), causes death from carbonic oxide poisoning. An atmosphere containing 0·2 per cent. renders a man helpless and unconscious in about half an hour. A mouse, owing to its small size, succumbs in one-twentieth of the time. Carbon monoxide in contact with caustic potash at a high temperature produces potassium formate, thus:

$$\underset{\text{Caustic potash.}}{KHO} + \underset{\text{Carbon monoxide.}}{CO} = \underset{\text{Potassium formate.}}{KCHO_2}$$

Carbon monoxide when passed over finely divided nickel or iron gently heated, combines with these metals to form vapours which condense to liquids; nickel carbonyl, which is colourless, has the formula $Ni(CO)_4$. If the vapour of nickel carbonyl be passed through a glass tube heated to 200° it is decomposed, and the nickel is deposited on the glass as a bright mirror-like coating.

Test.—Carbon monoxide gives no precipitate with lime-water, but on applying a light it burns with a pale blue flame, and the resulting gas (carbon dioxide) then produces a precipitate with lime-water.

CO is an unsaturated compound.

CARBON DIOXIDE

of $CO<^{Cl}_{Cl}$ phosgene gas

Formula, CO_2; *molecular weight*, 44;
liquefies —78°.

Also known as *carbonic anhydride*, *carbonic acid gas*, and *choke-damp*. It is always formed when carbon in any form, or any compound of carbon, is burnt with a free supply of air. It is one of the gases evolved from volcanoes, and in certain instances from fissures in the earth, as in the Grotto del Cane near Naples, and in the poison valley of Java.

Modes of preparation.—(i) It is most easily prepared by the action of hydrochloric acid on calcium carbonate in the form of marble or chalk.

by HCl + Ca

$CaCO_3$	+	$2HCl$	=	$CaCl_2$	+	CO_2	+	H_2O
Calcium carbonate.		Hydrochloric acid.		Calcium chloride.		Carbon dioxide.		Water.

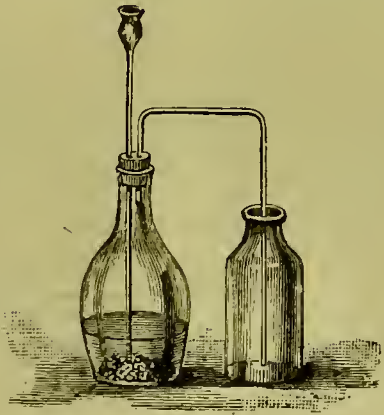


Fig. 18.—Preparation and collection of Carbon Dioxide.

or H_2SO_4 + CaCO

It may be collected in the pneumatic trough over water, or, since it is heavier than air, it can be collected by downward displacement of air (Fig. 18).

Sulphuric acid may be substituted for hydrochloric acid, but in this case the insoluble calcium sulphate forms a coating over the marble or chalk, and is apt to stop the evolution of the gas.

$CaCO_3$	+	H_2SO_4	=	$CaSO_4$	+	CO_2	+	H_2O
Calcium carbonate.		Sulphuric acid.		Calcium sulphate.		Carbon dioxide.		Water.

(ii) Carbon dioxide is evolved by heating chalk or limestone, as in the preparation of lime in the limekilns.

$CaCO_3$	=	CaO	+	CO_2
Calcium arbonate.		Lime.		Carbon dioxide.

(iii) Carbon dioxide is also evolved by heating a bicarbonate, such as sodium or potassium bicarbonate.

$$\underset{\text{Sodium bicarbonate.}}{2NaHCO_3} = \underset{\text{Sodium carbonate.}}{Na_2CO_3} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

(iv) By burning carbon monoxide in oxygen or in air, carbon dioxide is produced.

$$\underset{\text{Carbon monoxide.}}{2CO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Carbon dioxide.}}{2CO_2}$$

Properties.—The specific gravity of carbon dioxide is 22, and it is heavier than air; it is a colourless gas, possessing a peculiar faint pungent odour in quantity, and a faint acid taste; it is not combustible, neither is it a supporter of combustion, a lighted taper being immediately extinguished when lowered into the gas. It can be liquefied by a pressure of 38·5 atmospheres at 0°, and if the liquid is allowed to escape into the air, the portion that evaporates so lowers the temperature of the remaining portion that it solidifies. It is slightly soluble in water, as at ordinary temperatures water dissolves its own volume of the gas; under a pressure of two atmospheres water will dissolve twice its volume of the gas, under a pressure of three atmospheres three times its volume, under a pressure of four atmospheres four times its volume, and so on. So that if a pint bottle of soda-water that has been charged under a pressure of four atmospheres be opened, three pints of the gas will escape with effervescence, one pint remaining in solution, since there is still the ordinary pressure of the atmosphere upon the water. The solution of carbon dioxide in water faintly reddens blue litmus paper, the liquid probably containing true carbonic acid (H_2CO_3), thus :

$$\underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Carbonic}\\\text{acid.}}}{H_2CO_3}$$

It is for this reason that carbon dioxide is also called carbonic anhydride (the anhydride of carbonic acid) and carbonic acid gas. Carbon dioxide is not a poison if swallowed into the stomach, as in the form of effervescent waters and drinks it is taken in considerable quantities, but if *inhaled* in quantity it produces death from suffocation, not that it unites with the hæmoglobin of the blood, but because it dilutes down and keeps out the necessary oxygen of the air. After explosions in coal-mines, it is the carbon dioxide, mixed with some carbon monoxide (choke-damp), produced by the explosion of the marsh gas or fire-damp with the air, that causes in so many cases the suffocation of the miners. Since carbon dioxide is evolved, as previously mentioned, from limekilns, it is not an uncommon occurrence for tramps and others sleeping close to a limekiln for the sake of the warmth, to die in their sleep, suffocated by this gas. If pure carbon dioxide is inhaled, it produces spasm of the glottis and consequent death from asphyxia, unless the inhalation of the gas is immediately stopped. Carbon dioxide, as previously explained, is largely used in the so-called aërated waters, to give to them their effervescent character and their pleasant sharp taste.

Carbon dioxide, if passed into a solution of an alkali, forms first a carbonate, and then converts the carbonate into a bicarbonate. Thus, with caustic potash it first forms potassium carbonate.

$$\underset{\substack{\text{Caustic}\\\text{potash.}}}{2KHO} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} = \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} + \underset{\text{Water.}}{H_2O}$$

Sub acetate of [illegible],
Baryta water

By its further action it converts the carbonate into the bicarbonate.

$$\begin{array}{ccccccc} K_2CO_3 & + & CO_2 & + & H_2O & = & 2KHCO_3 \\ \text{Potassium carbonate.} & & \text{Carbon dioxide.} & & \text{Water.} & & \text{Potassium bicarbonate.} \end{array}$$

Carbon dioxide passed into lime-water (solution of calcium hydrate) first renders it turbid by precipitating calcium carbonate.

$$\begin{array}{ccccccc} Ca(HO)_2 & + & CO_2 & = & CaCO_3 & + & H_2O \\ \text{Calcium hydrate.} & & \text{Carbon dioxide.} & & \text{Calcium carbonate.} & & \text{Water.} \end{array}$$

By its further action it converts the insoluble calcium carbonate into the soluble bicarbonate, and so renders the liquid clear again.

$$\begin{array}{ccccccc} CaCO_3 & + & CO_2 & + & H_2O & = & Ca(HCO_3)_2 \\ \text{Calcium carbonate.} & & \text{Carbon dioxide.} & & \text{Water.} & & \text{Calcium bicarbonate.} \end{array}$$

Test.—Carbon dioxide turns lime-water turbid or milky when shaken up with it.

CARBON OXYCHLORIDE.

OCl ✓ *Formula*, $COCl_2$. Phosgene Gas.

Also known as *carbonyl chloride* and *phosgene gas* (so named on account of its being produced by the action of light).

1. This body may be regarded either as carbon monoxide united with chlorine, or
2. as carbon dioxide from which one atom of oxygen has been displaced by two atoms of chlorine.

Mode of preparation.—It is produced when equal volumes of carbon monoxide and chlorine are exposed to direct sunlight, thus :

Co + Cl.

$CO < Cl + 2NH_3 = CO < NH_2 +$

$$\underset{\text{Carbon monoxide.}}{CO} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Carbon oxychloride.}}{COCl_2}$$

When the two gases unite, the volume of the mixed gases diminishes to one-half.

$$CO + Cl_2 = COCl_2$$

1 molecule + 1 molecule = 1 molecule.
∴ 1 volume + 1 volume = 1 volume.

NH_3 By the action of ammonia on this substance urea is formed. a synthetic way of forming ur[illegible] ammonia + phosgene gas

$$\underset{\text{Carbon oxychloride.}}{COCl_2} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\text{Hydrogen chloride.}}{2HCl}$$

CARBON BISULPHIDE OR DISULPHIDE.

CS

Formula, CS_2.

This body may be regarded as carbon dioxide in which the oxygen has been displaced by sulphur, and just as carbon dioxide is produced by burning carbon in oxygen, so carbon bisulphide is produced by burning carbon in sulphur vapour.

Mode of preparation.—By passing the vapour of sulphur over red-hot charcoal, and then conveying the vapour of the bisulphide of carbon through a spiral tube kept cool by immersion in water, by which means the bisulphide of carbon condenses to a liquid.

Properties.—Bisulphide of carbon is a colourless, mobile, very volatile liquid. When first prepared it possesses a very disagreeable odour, from which it can, to a great extent, be purified by shaking with mercury and corrosive sublimate, and redistilling. It is heavier than water, and after agitation with water it sinks to the bottom, leaving a very small quantity dissolved in the water. It is a very inflammable liquid, boils at 46°, and the vapour takes fire at 149°, so that it can be lighted by a tube of hot paraffin wax. It forms carbon dioxide and sulphur dioxide when burnt.

$$\underset{\substack{\text{Carbon}\\\text{bisulphide.}}}{CS_2} + \underset{\text{Oxygen.}}{3O_2} = \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{2SO_2}$$

Carbon bisulphide is used for many technical purposes, as it is an excellent solvent of many bodies, possessing the property of dissolving sulphur, phosphorus, fats, resins, and india-rubber.

With certain of the metallic sulphides carbon disulphide will unite, forming sulphocarbonates, which may be regarded as carbonates in which the oxygen has been displaced by sulphur, thus with potassium sulphide it forms potassium sulphocarbonate.

$$\underset{\substack{\text{Potassium}\\\text{sulphide.}}}{K_2S} + \underset{\substack{\text{Carbon}\\\text{disulphide.}}}{CS_2} = \underset{\substack{\text{Potassium}\\\text{sulphocarbonate.}}}{K_2CS_3}$$

SILICON.

Symbol, Si ; *tetrad ; atomic weight*, 28.

Silicon is widely and abundantly distributed in nature, but not in the free state. Next to oxygen it is the chief constituent of the earth's crust, just as the closely related element carbon is the chief constituent of organic bodies. The oxide of silicon (silica) occurs both free and in combination with bases as the various natural silicates.

Preparation of silicon.—The element silicon may be obtained by heating the double fluoride of potassium and silicon ($2KF, SiF_4$) with the metal potassium, which abstracts the fluorine from its combination with the silicon, setting free that element. Prepared in this way, silicon is obtained as a dark brown amorphous powder. It may, however, be obtained in the crystalline condition by heating for some time the same ingredients, viz. the double fluoride of potassium and silicon, and the metal potassium, with the metal zinc; on cooling, an ingot of zinc is obtained with crystals of silicon embedded in it; by treating this with hydrochloric acid, the zinc is dissolved, leaving very hard steel-grey crystals; there seems, however, to be some doubt as to this substance being pure silicon. Silicon forms an inflammable gas with hydrogen (SiH_4) and combines, when heated with dry hydrogen chloride, to form $SiHCl_3$. These two substances have formulæ analogous to marsh gas (CH_4) and choloroform ($CHCl_3$).

SILICA.

Formula, SiO_2

Also known as *oxide of silicon* and *silicic anhydride.*

Silica occurs in the free state in nature as *rock crystal* (usually in six-sided prisms), *quartz*, *flint*, *sand*, *sandstone*, *agate*, *opal*, *jasper*, and *amethyst.* The so-called *infusorial earth*, or the inorganic remains of certain infusoria, consists essentially of amorphous silica. Silica is also present in the stems of certain grasses, cereals, and rushes, and in the feathers of many birds. Silica is insoluble in water and in all acids except hydrofluoric.

SILICIC ACID.

There are several varieties of silicic acid—metasilicic acid (H_2SiO_3), orthosilicic acid (H_4SiO_4), parasilicic acid (H_6SiO_5), etc.

Natural silicates.—*Clay*, or aluminium silicate ($Al_2Si_2O_7 + 2H_2O$), is the most widely distributed of the natural silicates; the colour of common or brown clay is due to iron contained in it. Clay in its purest form occurs as *kaolin* or *china-clay*, and is produced from a felspar, a double silicate of aluminium and potassium, by the action of the carbon dioxide of the air, which unites with the potassium to form potassium carbonate, which is washed away, leaving the silicate of aluminium in a white state.

Amongst other silicates may be named *meerschaum*, *French chalk*, *asbestos*, *pumice*, etc.

Pure silica can be obtained from sand and from most silicates by fusing with three to four times its weight of sodium carbonate in a platinum dish and extracting the fused mass with water; on adding hydrochloric acid to the clear solution, silicon hydrate ($Si(HO)_4$) is precipitated in gelatinous flocks. This is filtered off, washed, and made red hot, when it is left as pure white silica (SiO_2).

Glass.—Glass may be defined as an amorphous mixture of various silicates nearly insoluble in water. Glass contains (1) silica, (2) soda or potash, (3) lime or lead oxide.

Crown glass, common window glass, bottle glass, or *soda glass* is made by fusing together chalk ($CaCO_3$), sodium carbonate (Na_2CO_3), and sand (SiO_2). It consists of calcium and sodium silicates; the green colour of common bottle glass is due to iron derived from the sand, and existing in the glass as ferrous silicate; the colour can be removed by adding to the melted glass a small quantity of manganese dioxide, which oxidises the green ferrous silicate to the almost colourless ferric silicate.

Hard glass or *potash glass* contains potassium in the place of sodium, and is made by fusing together chalk, potassium carbonate, and sand. It consists of calcium and potassium silicates, and requires a much higher temperature to melt it than soda glass; it is therefore useful in the manufacture of hard glass-tubing, and of chemical apparatus required to stand a high temperature.

Flint glass or *crystal glass* is a potash glass containing lead in the place of calcium, and is made by fusing together potassium carbonate (K_2CO_3), litharge or lead oxide (PbO), and sand (SiO_2). It consists of potassium and lead silicates, and is distinguished by its lustre and refractive power, hence it is valuable for optical purposes.

Soluble glass is either sodium or potassium silicate, generally the former. The sodium silicate is prepared by fusing together sodium carbonate and sand. It is a thick, syrupy liquid, miscible with, or soluble in, water; if painted over a surface, such as a wall, it is decomposed by the carbon dioxide of the air, a film of silica, or of a silicate, being left as a hard protective surface on the wall.

Coloured glasses are made by the addition of different metallic oxides to glass while in a molten condition. Blue glass is made by adding oxide of cobalt; red glass by adding cuprous oxide.

Porcelain and earthenware.—Porcelain and earthenware articles consist of clay that has been moulded into the required shapes, then baked hard, and afterwards covered with some substance that fuses at a high temperature, and forms a glaze, thus preventing the passage of liquids through what would otherwise be a porous medium. The glaze used for the finer kinds of porcelain is generally produced by dipping the unglazed article into water containing powdered felspar suspended in it; on draining the article the water sinks into the porous substance, leaving a film of felspar over its surface, and on strongly heating the article in a furnace this film of felspar melts and forms the glaze. Common earthenware, which is of a reddish-brown colour, is frequently glazed with litharge (oxide of lead), which forms an easily fusible lead silicate on the application of heat, this lead silicate constituting the glaze; if acid articles of food, such as vinegar, lemon-juice, lime-juice, etc., be kept in such vessels, the lead may be dissolved by the acid, and so the glaze may become a source of lead poisoning. Another very perfect glaze is *salt glaze;* common salt (sodium chloride) is thrown into the furnace containing the strongly-heated articles, the sodium chloride volatilises and is decomposed by the intense heat and the water vapour in the furnace. The sodium oxide formed condenses on the surface and forms a fusible silicate with the clay.

$$\underset{\text{Salt.}}{2NaCl} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sodium}\\\text{oxide.}}}{Na_2O} + \underset{\substack{\text{Hydrogen}\\\text{chloride.}}}{2HCl}$$

BORON.

Symbol, B; *triad; atomic weight*, 11.

Boron does not occur in nature in the free state, but is found as free boric acid, and also in the form of various natural borates. In some respects its compounds resemble those of the metal aluminium.

Preparation of boron.—Amorphous boron is obtained, as a brown powder, by heating boron trioxide (B_2O_3) with sodium. Crystalline boron is prepared by melting the amorphous variety in aluminium, and when cold dissolving away the aluminium; it has been proved to be a compound of aluminium and boron.

BORIC OR BORACIC ACID.

Formula, H_3BO_3.

Boracic acid is found in the jets of steam known as *soffioni* issuing from fissures in the earth in the volcanic districts of Tuscany; these jets of steam condense and form small lagoons, by the concentration of the water of which boracic acid is obtained. Since this volcanic boracic acid is always accompanied by salts of ammonia, it is possible that it is produced deep down in the earth by the contact of boron nitride with steam, as these two bodies are known to decompose one another as follows :—

$$\underset{\text{Boron nitride.}}{BN} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Boracic acid.}}{H_3BO_3} + \underset{\text{Ammonia.}}{NH_3}$$

Boracic acid may also be prepared by mixing together a concentrated hot solution of borax with sulphuric or hydrochloric acids ; on cooling, the boracic acid crystallises out.

$$\underset{\text{Borax.}}{Na_2B_4O_7} + \underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Water.}}{5H_2O} = \underset{\text{Boric acid.}}{4H_3BO_3} + \underset{\text{Sodium chloride.}}{2NaCl}$$

Properties.—Boracic acid is a white solid, crystallising in small soapy-feeling crystals, very soluble in hot, and moderately soluble in cold water. It possesses antiseptic properties, and is used as an antiseptic dressing and as a preservative.

On gently heating boracic acid, each molecule of the acid loses a molecule of water, and metaboric acid is formed.

$$\underset{\text{Boracic acid.}}{H_3BO_3} = \underset{\text{Metaboracic acid.}}{HBO_2} + \underset{\text{Water.}}{H_2O}$$

If further heat be applied, pyroboric acid ($H_2B_4O_7$) is produced, and finally all the water is driven off and boracic anhydride or boron trioxide (B_2O_3) is left, thus:

$$\underset{\text{Metaboracic acid.}}{2HBO_2} = \underset{\text{Boracic anhydride.}}{B_2O_3} + \underset{\text{Water.}}{H_2O}$$

Tests.—(i) If boracic acid be mixed with some alcohol, and a light applied to the mixture, the boracic acid communicates a green colour to the flame of the burning alcohol.

(ii) If yellow turmeric paper be dipped into a solution of boracic acid and dried at 100° it turns reddish brown. On adding ammonia the colour turns dark blue. It is the only acid that turns turmeric brown, this colour being usually produced by alkalies.

BORAX.

Sodium pyrobora

Formula, $Na_2B_4O_7, 10H_2O$.

This is pyroborate of sodium. Borax occurs native as *tincal* in Persia and elsewhere; of late, borax has been found in large quantities in California.

Preparation of borax.—If the crude volcanic boracic acid be heated with sodium carbonate, ammonium carbonate volatilises (*see* page 123), and borax remains.

$$\underset{\text{Sodium carbonate.}}{Na_2CO_3} + \underset{\text{Boric acid.}}{4H_3BO_3} = \underset{\text{Borax.}}{Na_2B_4O_7} +$$

uses of borax

$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{6H_2O}$$

Borax when heated gives off its water of crystallisation, swelling up enormously (*intumescence*), and then melts; fused borax dissolves many metallic oxides, and often acquires thereby characteristic colours; thus, cobalt gives a blue borax bead, chromium a green bead, etc. For the same reason it is largely used in the operation of "brazing," for uniting pieces of brass, silver, gold, etc.; the melted borax dissolves any oxide, and offers a clean metallic surface to which the solder adheres.

Tests.—(i) If sulphuric acid be added to borax (to set free boracic acid), the mixture stirred with alcohol, and a light applied, a green-coloured flame will be obtained.

(ii) If to a solution of borax, hydrochloric acid be added, the solution will give the turmeric paper test (*see* p. 170).

P + As – 4 atoms in molecule.

CHAPTER X.

PHOSPHORUS—COMPOUNDS OF PHOSPHORUS.

Phosphorus—Ordinary or Yellow Phosphorus—Red or Amorphous Phosphorus—Phosphorus Trioxide—Phosphorus Pentoxide—Phosphoric Acid — Pyrophosphoric Acid — Metaphosphoric Acid—Phosphorous Acid—Hypophosphorous Acid—Gaseous Phosphoretted Hydrogen—Liquid Phosphoretted Hydrogen—Compounds of Phosphorus and Chlorine—Compounds of Phosphorus and Bromine—Compounds of Phosphorus and Iodine.

PHOSPHORUS.

Symbol, P; *molecule*, P_4; *pentad; atomic weight*, 31; *molecular weight*, 124.

PHOSPHORUS and arsenic are the only two elements that contain four atoms in the molecule; the density of phosphorus vapour is 62, therefore its molecular weight is $62 \times 2 = 124$, and as the relative weight of its atom is 31, the molecule must contain four atoms.

Phosphorus (from φῶς, *light;* φέρειν, *to bear*) derives its name from its property of shining, or being luminous, in the dark; it occurs in nature principally as calcium phosphate in the minerals *apatite* and *phosphorite*, and in soils in small quantities; plants possess the power of abstracting the calcium phosphate from soils, and of storing it in their tissues partly in the form of a soluble calcium phosphate, and partly in the form of complex organic bodies containing phosphorus; animals by using plants as foods convey phosphorus into their systems, and the calcium phosphate becoming deposited in bones constitutes the principal inorganic and hardening constituent of bones, whilst phosphorus in the form of complex organic bodies is an essential constituent of the brain, nervous, and other tissues; in our food more phosphorus is taken than the system requires, the excess being got rid of mainly by excretion as phosphates (principally in the urine, partly in the fæces), and thus returned to the soil. Phosphorus was first prepared (1670) from the calcium phosphate obtained from concentrated urine; later, the discovery was made that bones also contain calcium phosphate, and it is from this source that phosphorus is now prepared.

There are two allotropic forms of phosphorus, the *ordinary* or *yellow*, and the *red* or *amorphous*, which differ remarkably from one another in their properties.

ORDINARY OR YELLOW PHOSPHORUS.

This is prepared from bones in the following manner:—(i) The bones are calcined to obtain bone-ash, an impure calcium phosphate; (ii) the bone-ash is digested with sulphuric acid. Phosphoric acid remains in solution and calcium sulphate is precipitated.

$$\underset{\text{Calcium phosphate.}}{Ca_3(PO_4)_2} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} = \underset{\text{Calcium sulphate.}}{3CaSO_4} + \underset{\text{Phosphoric acid.}}{2H_3PO_4}$$

The liquid is filtered and evaporated to a syrup; 25 per cent. of charcoal powder is added, and the mixture dried; it is finally distilled at a red heat from clay retorts, and the phosphorus vapour collected under water.

The reactions which occur are:—(1) the phosphoric acid gives off water and is converted into metaphosphoric acid.

$$\underset{\text{Phosphoric acid.}}{H_3PO_4} = \underset{\text{Water.}}{H_2O} + \underset{\text{Metaphosphoric acid.}}{HPO_3}$$

(2) The metaphosphoric acid is reduced by the red-hot carbon.

$$\underset{\text{Metaphosphoric acid.}}{4HPO_3} + \underset{\text{Carbon.}}{12C} = \underset{\text{Carbon monoxide.}}{12CO} + \underset{\text{Hydrogen.}}{2H_2} + \underset{\text{Phosphorus.}}{P_4}$$

(iii) The phosphorus so obtained is purified by forcing it, when melted under hot water, through wash-leather; the purified phosphorus is then cast into sticks, and kept under cold water.

Properties.—Phosphorus is a colourless transparent solid when first prepared, somewhat resembling white wax in appearance and consistency, but it gradually becomes yellowish in colour by keeping. It melts at 44° (110° F.), ignites at a slightly higher temperature, boils at 269°, and out of contact with air may be distilled unchanged; it is luminous in the dark and, if exposed to the air at ordinary temperatures, it gives off, without igniting, white fumes of phosphorus trioxide or phosphorous anhydride (P_4O_6); when burnt, it forms a white powder, the phosphorus pentoxide or phosphoric anhydride (P_2O_5). If phosphorus be held in the hands for a short time, it is very apt to catch fire, and it is therefore kept under water. It is slightly soluble in ether and in the fixed oils, and is very soluble in carbon bisulphide; if its solution in this substance be poured on a sheet of paper or on the floor, the carbon bisulphide rapidly evaporates, and the phosphorus is left in so fine a state of division that it ignites spontaneously in a very short time. Phosphorus is very poisonous, and is a common constituent of the *rat-pastes*, which consist of yellow phosphorus, fat, sugar, flour, and prussian blue; most cases of phosphorus poisoning are due to the swallowing of rat-paste.

RED OR AMORPHOUS PHOSPHORUS.

This is prepared by heating ordinary phosphorus in an atmosphere of carbon dioxide or of nitrogen to 240° for some time, any ordinary phosphorus which remains unchanged being removed by dissolving it out with carbon disulphide. It is also very slowly formed by the exposure of a stick of phosphorus, kept under water, to light, when, after some time, a red coating of amorphous phosphorus forms on the stick.

If amorphous phosphorus be heated (while in an atmosphere of carbon dioxide or of nitrogen) to a high temperature, it passes into vapour which condenses as ordinary phosphorus.

Properties.—This allotropic form of phosphorus is a red-brown amorphous powder; it does not fume in the air, nor is it luminous in the dark; it does not melt at 250°, and catches fire only at 260°; there is therefore no necessity for keeping it under water; it is insoluble in carbon bisulphide, and all liquids; it is odourless and non-poisonous; although usually amorphous it has been obtained in crystals.

Use of phosphorus in lucifer matches.—Both varieties of phosphorus are used in the manufacture of lucifer matches. Common matches are tipped with a mixture containing ordinary phosphorus, and ignite when rubbed on any rough surface, the friction producing sufficient heat to set the phosphorus on fire. *Safety matches* have no phosphorus on their tips, but are tipped with a mixture of potassium chlorate, red lead, and black sulphide of antimony, the phosphorus being on the side of the box in the form of amorphous phosphorus, stuck on with common glue; when a safety match is rubbed against this, the portion of amorphous phosphorus rubbed adheres to the tip of the match and causes it to catch fire.

The following table contrasts the different properties of the two allotropic forms of phosphorus:—

Ordinary Phosphorus.	**Amorphous Phosphorus.**
Form.—In sticks.	In powder.
Colour.—Colourless, or yellow.	Red-brown.
Odour.—Peculiar.	None.
Luminosity. — Luminous in dark.	Not luminous.
Inflammability. — Ignites at 45° C., and is apt to ignite when handled.	Ignites at 260° C., and may be handled with impunity.
Exposure to air.—White fumes evolved.	No fumes evolved
Solubility.—Soluble in carbon bisulphide, and slightly so in ether and the fixed oils.	Insoluble in all liquids.
Physiological action. — Very poisonous.	Not poisonous.

COMPOUNDS OF PHOSPHORUS AND OXYGEN.

There are two oxides of phosphorus, viz. phosphorous oxide or phosphorous anhydride (P_4O_6), and phosphoric oxide or phosphoric anhydride (P_2O_5).

PHOSPHOROUS OXIDE.

or phosphorous anhydride

Formula, P_4O_6.

O6

14

When phosphorus is burnt in a rapid current of air a mixture of the two oxides P_4O_6 and P_2O_5 is formed, the mixture is passed through a glass tube surrounded with hot water at 60°; the P_2O_5 condenses in this tube, while the more volatile P_4O_6 passes on and is condensed in a U-tube surrounded with a freezing mixture. It is a soft, waxlike, crystalline solid, melting at 22·5°; it gives off a very poisonous vapour. When warmed in oxygen it bursts into flame. Its vapour density is 110, and its molecular weight 220.

PHOSPHORUS PENTOXIDE.

phosphoric oxide or phosphoric anhydride

Formula, P_2O_5.

This oxide is obtained as a white powder by burning phosphorus in oxygen, or in a free supply of air. At a high temperature it can be volatilised; it has a very powerful attraction for moisture, being one of the most hygroscopic substances known. It is the anhydride of phosphoric acid, and if dissolved in hot water it forms phosphoric acid at once; if dissolved in cold water it forms at first metaphosphoric acid: the metaphosphoric acid then gradually unites with more water to form ordinary phosphoric acid.

ACIDS OF PHOSPHORUS.

There are three acids of phosphorus, viz.:

H_3PO_4	Phosphoric acid.
H_3PO_3 or H_2PHO_3	Phosphorous acid.
H_3PO_2 or HPH_2O_2	Hypophosphorous acid.

Of phosphoric acid there are two derivatives, viz. pyrophosphoric acid ($H_4P_2O_7$) and metaphosphoric acid (HPO_3), which consist of phosphoric acid deprived of different amounts of water; these, however, are not separate acids of phosphorus, but are derivatives or varieties of phosphoric acid, in connection with which they will be described.

PHOSPHORIC OR ORTHO-PHOSPHORIC ACID.

Formula, H_3PO_4.

This is the ordinary or common phosphoric acid, and is called ortho-phosphoric acid (ὀρθός, *true*) in order to distinguish it from its two derivatives.

Modes of preparation.—(i) By dissolving phosphoric anhydride in hot water.

$$\underset{\text{Phosphoric anhydride.}}{P_2O_5} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Phosphoric acid.}}{2H_3PO_4}$$

(ii) The phosphoric acid used in medicine is obtained by boiling together for some time phosphorus, nitric acid, and water; the phosphorus is oxidised by the nitric acid to phosphoric anhydride, and this with the boiling water forms phosphoric acid.

$$\underset{\text{Phosphorus.}}{3P_4} + \underset{\text{Nitric acid.}}{20HNO_3} + \underset{\text{Water.}}{8H_2O} = \underset{\text{Phosphoric acid.}}{12H_3PO_4} + \underset{\text{Nitrogen dioxide.}}{20NO}$$

(iii) Phosphoric acid may be obtained by the action of phosphorus pentachloride on water, the hydrochloric acid being driven off by subsequent evaporation.

$$\underset{\text{Phosphorus pentachloride.}}{PCl_5} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Phosphoric acid.}}{H_3PO_4} + \underset{\text{Hydrochloric acid.}}{5HCl}$$

(iv) By the action of sulphuric acid on bone ash (*see* p. 173).

Properties.—Phosphoric acid is one of the least volatile inorganic acids, as it even expels sulphuric acid from its compounds. It forms three sodium salts, viz. Na_3PO_4, Na_2HPO_4, and NaH_2PO_4; the last-mentioned salt is acid to test-paper.

Tests.—(i) Phosphoric acid when neutralised with ammonia gives a canary-yellow precipitate of silver phosphate with solution of silver nitrate; this precipitate is readily dissolved, both by solution of ammonia and by nitric acid.

(ii) If to phosphoric acid excess of ammonia be added, and then solutions of ammonium chloride and am Cl + am OH +

magnesium sulphate, a white crystalline precipitate will form on shaking the mixture; this precipitate is the magnesium ammonium phosphate ($MgNH_4PO_4$).

MgSO
= white
pt

(ii) If a small quantity of a phosphate be boiled with strong nitric acid and ammonium molybdate, a bright yellow precipitate is formed.

HNO_3 + am
molybdate
yellow

PYROPHOSPHORIC ACID.

Formula, $H_4P_2O_7$.

This derivative of phosphoric acid is obtained by heating that acid a little above 200°; two molecules of phosphoric acid lose one molecule of water, forming pyrophosphoric acid.

$$\underset{\text{Phosphoric acid.}}{2H_3PO_4} - \underset{\text{Water.}}{H_2O} = \underset{\text{Pyrophosphoric acid.}}{H_4P_2O_7}$$

It may also be obtained in the form of its sodium salt by heating ordinary sodium phosphate, thus:

$$\underset{\text{Sodium phosphate.}}{2Na_2HPO_4} = \underset{\text{Sodium pyrophosphate.}}{Na_4P_2O_7} + \underset{\text{Water.}}{H_2O}$$

Tests.—(i) When neutralised with ammonia, pyrophosphoric acid gives a white precipitate with silver nitrate, thus distinguishing it from phosphoric acid, which gives a yellow precipitate.

white
with
Ag

(ii) Pyrophosphoric acid does not coagulate albumen, thus distinguishing it from metaphosphoric acid. (*See* below.)

Does
coagu
albu

METAPHOSPHORIC ACID.

Formula, HPO_3.

This variety of phosphoric acid can be prepared by heating that acid to redness; one molecule of phosphoric acid loses one molecule of water, forming metaphosphoric acid, thus :

$$\underset{\text{Phosphoric acid.}}{H_3PO_4} - \underset{\text{Water.}}{H_2O} = \underset{\text{Metaphosphoric acid.}}{HPO_3}$$

Metaphosphoric acid is obtained as a vitreous mass, and hence is known as *glacial phosphoric acid ;* it dissolves in water, and its solution changes slowly at ordinary temperatures, but rapidly with heat, into ordinary phosphoric acid.

Tests.—(i) When neutralised with ammonia, metaphosphoric acid gives a white precipitate with silver nitrate, thus distinguishing it from ordinary phosphoric acid, which gives a yellow precipitate.

(ii) If some unboiled white of egg be shaken with metaphosphoric acid, the albumen is coagulated ; this test distinguishes metaphosphoric acid from pyrophosphoric acid, which does not possess the power of coagulating albumen.

PHOSPHOROUS ACID.

Formula, H_3PO_3.

This acid contains in the molecule one atom of oxygen less than phosphoric acid.

Modes of preparation.—(i) By dissolving phosphorous oxide in cold water.

$$\underset{\text{Phosphorous anhydride.}}{P_4O_6} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Phosphorous acid.}}{4H_3PO_3}$$

(ii) By the action of phosphorus trichloride on water.

$$\underset{\text{Phosphorus trichloride.}}{PCl_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Phosphorous acid.}}{H_3PO_3} + \underset{\text{Hydrochloric acid.}}{3HCl}$$

H_3PO_3
H_2SO_3
H_2S

Properties.—Phosphorous acid has a very strong attraction for oxygen, and if exposed to the air forms phosphoric acid; on account of its affinity for oxygen it is a powerful reducing agent.

HYPOPHOSPHOROUS ACID.

Formula, H_3PO_2 or HPH_2O_2.

This acid contains one atom of oxygen less in the molecule than phosphorous acid; it is a monobasic acid, and its constitutional formula is therefore HPH_2O_2. It may be prepared by decomposing its barium salt (barium hypophosphite) with sulphuric acid, and filtering from the insoluble barium sulphate.

$$\underset{\substack{\text{Barium}\\\text{hypophosphite.}}}{Ba(PH_2O_2)_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Hypophosphorous}\\\text{acid.}}}{2HPH_2O_2} + \underset{\substack{\text{Barium}\\\text{sulphate.}}}{BaSO_4}$$

Preparation of the hypophosphites.—The sodium, potassium, calcium, and barium hypophosphites are prepared by boiling respectively the alkaline hydrate of the metal with phosphorus and water; in each case gaseous phosphoretted hydrogen is evolved. The two hypophosphites most employed in medicine are the sodium and calcium salts, the preparation of which is shown in the following equations:

$$\underset{\substack{\text{Sodium}\\\text{hydrate.}}}{3NaHO} + \underset{\text{Phosphorus.}}{P_4} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Sodium}\\\text{hypophosphite}}}{3NaPH_2O_2} + \underset{\substack{\text{Phosphoretted}\\\text{hydrogen.}}}{PH_3}$$

$$\underset{\substack{\text{Calcium}\\\text{hydrate.}}}{3Ca(HO)_2} + \underset{\text{Phosphorus.}}{2P_4} + \underset{\text{Water.}}{6H_2O} = \underset{\substack{\text{Calcium}\\\text{hypophosphite.}}}{3Ca(PH_2O_2)_2} + \underset{\substack{\text{Phosphoretted}\\\text{hydrogen.}}}{2PH_3}$$

COMPOUNDS OF PHOSPHORUS AND HYDROGEN.

There are three compounds of these elements, a gas (PH_3), a liquid (P_2H_4), and a solid (P_4H_2).

GASEOUS PHOSPHORETTED HYDROGEN OR PHOSPHINE.

Formula, PH_3.

Modes of preparation. — (i) As described above, this compound is produced when phosphorus is boiled with an alkali and water; the gas that is evolved is not, however, quite pure, since on coming in contact with the air it ignites spontaneously, whereas pure gaseous phosphoretted hydrogen is not spontaneously inflammable; its spontaneous inflammability, when prepared by the action of phosphorus on an alkali, is due to its being contaminated with a small quantity of the vapour of the liquid phosphoretted hydrogen, which is spontaneously inflammable.

(ii) The pure gas is obtained by the action of potassium hydroxide upon phosphonium iodide.

$$\underset{\text{Phosphonium iodide.}}{PH_4I} + \underset{\text{Potassium hydroxide.}}{KHO} = \underset{\text{Potassium iodide.}}{KI} + \underset{\text{Water.}}{H_2O} + \underset{\text{Phosphine.}}{PH_3}$$

It will be noticed that this equation is comparable with that on p. 119, by which ammonia is prepared. In fact, phosphine resembles ammonia in several respects: thus it combines directly with hydrogen chloride, bromide, and iodide to form salts (PH_4Cl, etc.), but it is not such a powerful base as ammonia.

Properties. — The specific gravity of phosphoretted hydrogen is 17, and it is somewhat heavier than air; it is a colourless gas, with a very unpleasant garlic-like odour, nearly insoluble in water, and igniting when a light is applied to it, forming by its combustion phosphorus pentoxide and water.

LIQUID PHOSPHORETTED HYDROGEN.

Formula, P_2H_4.

Preparation.—This body is obtained, mixed with PH_3, by the action of calcium phosphide on water.

$$\underset{\text{Calcium phosphide.}}{Ca_2P_2} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Phosphoretted hydrogen (liquid).}}{P_2H_4} + \underset{\text{Calcium hydrate.}}{2Ca(HO)_2}$$

Properties.—A liquid possessing a very unpleasant odour, and catching fire spontaneously on exposure to the air; it is very unstable, especially if exposed to sunlight, decomposing into the gaseous and solid phosphoretted hydrogen and free phosphorus.

Calcium phosphide is sometimes used as a signal at sea, since when thrown into water, the phosphoretted hydrogen evolved takes fire and burns with a bright light.

COMPOUNDS OF PHOSPHORUS AND CHLORINE.

There are two chlorides of phosphorus, a trichloride and a pentachloride.

PHOSPHORUS TRICHLORIDE OR PHOSPHOROUS CHLORIDE.

Formula, PCl_3.

A colourless liquid, fuming in moist air, and produced by burning phosphorus in chlorine, keeping the phosphorus in excess. Phosphorus trichloride is decomposed by water, with formation of phosphorous and hydrochloric acids.

$$\underset{\text{Phosphorus trichloride.}}{\mathrm{PCl_3}} + \underset{\text{Water.}}{\mathrm{3H_2O}} = \underset{\text{Phosphorous acid.}}{\mathrm{H_3PO_3}} + \underset{\text{Hydrochloric acid.}}{\mathrm{3HCl}}$$

Chlorine converts phosphorus trichloride into the pentachloride.

PHOSPHORUS PENTACHLORIDE OR PHOSPHORIC CHLORIDE.

Formula, PCl_5.

A white crystalline body, volatilising and fuming in the air. It is produced (i) by the action of chlorine on the trichloride of phosphorus; (ii) by burning phosphorus in excess of chlorine; (iii) by passing chlorine into a solution of phosphorus in carbon bisulphide. Phosphorus pentachloride is decomposed by water, with formation of phosphoric and hydrochloric acids.

$$\underset{\text{Phosphorus pentachloride.}}{\mathrm{PCl_5}} + \underset{\text{Water.}}{\mathrm{4H_2O}} = \underset{\text{Phosphoric acid.}}{\mathrm{H_3PO_4}} + \underset{\text{Hydrochloric acid.}}{\mathrm{5HCl}}$$

Phosphorus pentachloride is an extremely useful reagent, since it acts upon organic and inorganic bodies containing the hydroxyl group, replacing the HO by Cl.

$$\underset{\text{Sulphuric acid.}}{\mathrm{SO_2(HO)_2}} + \underset{\text{Phosphorus pentachloride.}}{\mathrm{PCl_5}} = \underset{\text{Phosphorus oxychloride.}}{\mathrm{POCl_3}} + \underset{\text{Hydrochloric acid.}}{\mathrm{HCl}} + \underset{\text{Chloro-sulphonic acid.}}{\mathrm{SO_2HOCl}}$$

$$\underset{\substack{\text{Acetic}\\\text{acid.}}}{\left\{\begin{matrix}CH_3\\COOH\end{matrix}\right.} + \underset{\substack{\text{Phosphorus}\\\text{pentachloride.}}}{PCl_5} = \underset{\substack{\text{Acetyl}\\\text{chloride.}}}{\left\{\begin{matrix}CH_3\\COCl\end{matrix}\right.} + \underset{\substack{\text{Phosphorus}\\\text{oxychloride.}}}{POCl_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl}$$

Phosphorus pentachloride has a vapour density at 300° of 52, instead of $(PCl_5\ 31 + 177{\cdot}5)\ \frac{208{\cdot}5}{2} = 104{\cdot}2$; this is explained by the fact that PCl_5 vapour does not exist; under ordinary conditions it dissociates into $PCl_3 + Cl_2$, so that we have two molecules, and must therefore divide the molecular weight by 4 instead of 2.

COMPOUNDS OF PHOSPHORUS WITH BROMINE AND IODINE.

There are two bromides of phosphorus, a tribromide (PBr_3), which is a liquid body, and a pentabromide (PBr_5), which is a solid body.

There are also two iodides of phosphorus, a di-iodide (P_2I_4), and a tri-iodide (PI_3), both solid bodies.

All these compounds are produced by direct combination between the elements.

The nitrogen group of elements.—Attention has already been called (p. 182) to the fact that phosphine can be prepared by a reaction comparable to that by which we obtain ammonia. This is but one instance of many points of resemblance between the elements nitrogen and phosphorus. In fact, the elements nitrogen, phosphorus, arsenic, antimony, and bismuth form a natural group. Thus they all (except bismuth) form gaseous compounds with hydrogen, having the formulæ NH_3, PH_3, AsH_3, SbH_3. Again, we have the corresponding acids, HNO_3, HPO_3, $HAsO_3$, $HSbO_3$; the metallic nature of the elements becomes more marked as the atomic weight increases, so that the oxides of bismuth do not form well-marked acids.

CHAPTER XI.

SULPHUR—OXIDES, ACIDS, AND COMPOUNDS OF SULPHUR.

Sulphur—Allotropic forms of Sulphur—Properties of Sulphur—Sulphur Dioxide or Sulphurous Anhydride—Sulphur Trioxide or Sulphuric Anhydride—Sulphurous Acid—Sulphuric Acid—Nordhausen or Fuming Sulphuric Acid—Sulphuretted Hydrogen—Hydrogen Persulphide—Thiosulphuric Acid—Compounds of Sulphur and Chlorine.

Exists free
Combined

SULPHUR.

Symbol, S; *molecule at* 500° S_6, *at* 1000° S_2; *hexad; atomic weight*, 32; *molecular weight*, 64 *at* 1000°.

Sulphur, commonly known as *brimstone*, occurs in nature in considerable quantities, in both the free and combined states. In the free state it is found in the volcanic districts of Sicily, Italy, and Iceland, in the form of yellow crystals, or in the amorphous state embedded in blue clay. In the combined state it exists as the various native metallic sulphides (*e.g. iron pyrites* FeS_2, *blende* ZnS, *black antimony* Sb_2S_3, *copper sulphide* CuS, *galena* PbS, *cinnabar* HgS), and as native metallic sulphates (*e.g. gypsum* $CaSO_4$, $2H_2O$, *Epsom salts*, $MgSO_4$, $7H_2O$, *heavy spar* $BaSO_4$). Sulphur is obtained from the rock, in which it occurs in volcanic districts, by melting it out; it is purified by distillation, the sulphur being converted into vapour, which is conducted into a large and cool brick chamber, in which it becomes cooled, and condenses, first to a yellow powder, *flowers of sulphur*, which subsequently melts, and is cast into sticks.

There are three allotropic forms of sulphur, viz.

two crystalline forms (the octahedral and the prismatic) and an amorphous form.

The allotropic forms of sulphur. — (i) *Octahedral variety.*—This is obtained by dissolving powdered stick sulphur in carbon bisulphide, and allowing the solution to evaporate spontaneously, when octahedral crystals of sulphur are deposited. Sulphur is found native crystallised in this form.

(ii) *Prismatic variety.*—This may be obtained by heating sulphur in a crucible until it melts, allowing it to cool until a crust forms on the surface, and then perforating the crust with an iron rod and pouring out the molten sulphur from underneath, when long prismatic crystals of sulphur will be found adhering to the sides of the crucible.

(iii) *Amorphous variety.*—This may be produced in two forms, plastic sulphur and precipitated sulphur. *Plastic sulphur* is prepared by heating sulphur to a temperature between 300° and 400°, and then pouring it into cold water, when it forms a plastic mass which can be drawn out like soft caoutchouc; it does not, however, retain its plasticity for long, as it gradually becomes hard and brittle, owing to its conversion into the crystalline condition. *Precipitated sulphur* is obtained by boiling flowers of sulphur with calcium hydrate (slaked lime) and water, when the sulphur passes into solution as calcium pentasulphide (CaS_5) and calcium thiosulphate (CaS_2O_3), from which solution the sulphur may be precipitated in the amorphous form by hydrochloric acid, which unites with the calcium and so sets free the sulphur.

$$\underset{\substack{\text{Calcium}\\\text{hydrate.}}}{3Ca(HO)_2} + \underset{\text{Sulphur.}}{6S_2} = \underset{\substack{\text{Calcium}\\\text{pentasulphide.}}}{2CaS_5} + \underset{\substack{\text{Calcium}\\\text{thiosulphate.}}}{CaS_2O_3} + \underset{\text{Water.}}{3H_2O}$$

$$\underset{\text{Calcium pentasulphide.}}{2CaS_5} + \underset{\text{Calcium thiosulphate.}}{CaS_2O_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Calcium chloride.}}{3CaCl_2} +$$

$$\underset{\text{Sulphur.}}{6S_2} + \underset{\text{Water.}}{3H_2O}$$

This is the process for preparing the *precipitated sulphur* of the British Pharmacopœia; if sulphuric acid is used instead of hydrochloric acid, calcium sulphate will be produced instead of calcium chloride, and, since the calcium sulphate is insoluble, will be thrown down with the precipitated sulphur. This mixture of calcium sulphate and sulphur used to be known as *milk of sulphur*, formerly an official preparation in the Pharmacopœia, but its use has been discontinued on account of the large quantity of insoluble sulphate present in it.

Properties.—Sulphur is a solid, possessing a pale yellow colour, odourless, tasteless, and insoluble in water; it burns with a pale blue flame, producing sulphur dioxide or sulphurous anhydride, a gas having a very pungent odour. At 115° sulphur melts to a clear mobile liquid, which, if allowed to cool, resolidifies to the ordinary yellow sulphur (the prismatic variety); if more strongly heated, it undergoes a peculiar change, for, instead of becoming more mobile, it becomes more viscid, and darker in colour, so that at 200° it is a dark brown liquid, and so viscid that the vessel containing it may be inverted without the sulphur flowing out; if heated above 200°, and up to 400°, it gradually becomes mobile again, and boils at 448°. Sulphur unites directly with oxygen, chlorine, phosphorus, carbon, and most of the metals. Sulphur is soluble in carbon disulphide.

Test.—Its yellow colour, combined with its burning with a pale blue flame, and producing the pungent

ff with or without effervescence which has the od
f rotten eggs & blackens lead paper.

smelling gas sulphur dioxide, renders the recognition of sulphur very easy.

COMPOUNDS OF SULPHUR AND OXYGEN.

There are two oxides of sulphur, viz. a gaseous oxide, sulphur dioxide or sulphurous anhydride (SO_2), and a solid oxide, sulphur trioxide or sulphuric anhydride (SO_3).

So
So

SULPHUR DIOXIDE OR SULPHUROUS ANHYDRIDE.

Liquefies at —10°.

O

This compound is contained in the gases of volcanoes.

Modes of preparation.—(i) By the combustion of sulphur in air or oxygen.

$$\underset{\text{Sulphur.}}{2S} + \underset{\text{Oxygen.}}{2O_2} = \underset{\text{Sulphur dioxide.}}{2SO_2}$$

(ii) By roasting iron pyrites in air.

$$\underset{\text{Iron pyrites.}}{4FeS_2} + \underset{\text{Oxygen.}}{11O_2} = \underset{\text{Ferric oxide.}}{2Fe_2O_3} + \underset{\text{Sulphur dioxide.}}{8SO_2}$$

(iii) For experimental purposes sulphur dioxide is most readily prepared by the action of strong sulphuric acid with heat on the metals copper, silver, or mercury.

$$\underset{\text{Copper.}}{Cu} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Copper sulphate.}}{CuSO_4} + \underset{\text{Sulphur dioxide.}}{SO_2} + \underset{\text{Water.}}{2H_2O}$$

(iv) Sulphur dioxide can be cheaply prepared by the action of strong sulphuric acid with heat on charcoal; it is not, however, pure, as it is mixed with carbon dioxide, which is produced at the same time.

$$\underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Charcoal.}}{C} = \underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{2H_2O}$$

Properties.—The specific gravity of sulphur dioxide is 32, and it is considerably heavier than air; it is a colourless gas, with a very pungent irritating odour, and an acid taste; it is neither combustible nor is it a supporter of combustion; it is very poisonous, and is freely soluble in water, 60 volumes dissolving in 1 volume of water. If cooled by means of a freezing mixture it condenses to a liquid; the apparatus for liquefying it is shown in Fig. 19. A is a flask in which the sulphur dioxide is prepared by heating strong sulphuric acid with copper. The gas is passed through a wash-bottle B, and then through a spiral

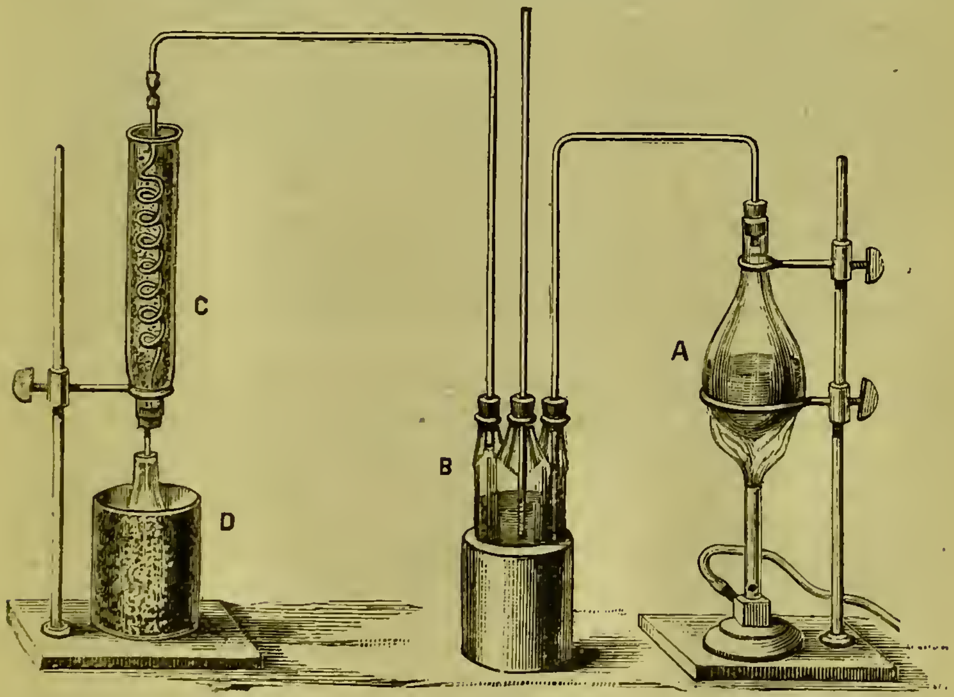


Fig. 19.—Preparation and Liquefaction of Sulphur Dioxide.

tube surrounded by a freezing mixture C, the liquefied gas being received in a flask D, which is also surrounded by a freezing mixture. Sulphur dioxide is a bleaching agent, and also an antiseptic, on account of its germicidal properties; as an antiseptic it is employed in the disinfection of rooms in which patients suffering from infectious fevers have been kept, but it is doubtful whether it is thoroughly reliable for such a purpose. For this purpose sulphur is heated in an iron saucepan until it has passed through the viscid stage and again become mobile (p. 189); it is then lighted in the room, the windows and the doors being closed; 1 to $1\frac{1}{2}$ lb. of sulphur are used to every 1,000 cubic feet of air space in the room.

If sulphur dioxide and sulphuretted hydrogen gases be mixed, a cloud of free sulphur is formed.

$$\underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{2SO_2} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{4H_2S} = \underset{\text{Sulphur.}}{3S_2} + \underset{\text{Water.}}{4H_2O}$$

It is possible that much of the sulphur found free in nature in volcanic districts is produced in this manner.

Tests.—(i) Its peculiar pungent and irritating odour.

Ou. (ii) It turns paper moistened with potassium bichromate bluish green. Emerald green test

(iii) It gives a blue colour with a mixture of iodic acid and starch.

SULPHUR TRIOXIDE OR SULPHURIC ANHYDRIDE.

Formula, SO_3.

SO_3

Modes of preparation.—(i) By passing a mixture of sulphur dioxide and oxygen over heated and finely divided platinum, when the two gases unite to form the higher oxide of sulphur.

$$\underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{2SO_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Sulphur}\\\text{trioxide}}}{2SO_3}$$

(ii) By gently heating Nordhausen or fuming sulphuric acid, when sulphuric anhydride volatilises over and condenses.

$$\underset{\substack{\text{Nordhausen}\\\text{sulphuric acid.}}}{H_2SO_4, SO_3} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} + \underset{\substack{\text{Sulphur}\\\text{trioxide.}}}{SO_3}$$

(iii) By distilling sulphuric acid with phosphoric anhydride.

$$\underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} + \underset{\substack{\text{Phosphoric}\\\text{anhydride.}}}{P_2O_5} = \underset{\substack{\text{Phosphoric}\\\text{acid.}}}{2H_3PO_4} + \underset{\substack{\text{Sulphuric}\\\text{anhydride.}}}{3SO_3}$$

Properties.—Sulphur trioxide is a solid body, occurring in white silky needles. It dissolves with avidity in water, uniting with it to form sulphuric acid.

$$\underset{\substack{\text{Sulphuric}\\\text{anhydride.}}}{SO_3} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4}$$

SULPHUROUS ACID.

Formula, H_2SO_3.

Mode of preparation.—By passing sulphurous anhydride into water.

$$\underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sulphurous}\\\text{acid.}}}{H_2SO_3}$$

Properties.—Sulphurous acid possesses the characteristic pungent odour of sulphurous anhydride. If exposed to the air oxygen is absorbed, and the sulphurous acid is slowly converted into sulphuric acid ($2H_2SO_3 + O_2 = 2H_2SO_4$). On account of this readiness to combine with oxygen, sulphurous acid is a powerful reducing agent. Nascent hydrogen can, however, reduce sulphurous acid, depriving it of all its oxygen, and setting free sulphuretted hydrogen ($H_2SO_3 + 3H_2 = H_2S + 3H_2O$). If sulphurous acid be neutralised with an alkaline hydrate or carbonate, a sulphite is produced. Sulphites are more easily prepared by the union of sulphurous anhydride with the strong bases; thus, if sulphurous anhydride be passed into solutions of caustic potash or caustic soda, sulphites of the metals are produced, thus:

$2NaHO$	+	SO_2	=	Na_2SO_3	+	H_2O
Caustic soda.		Sulphurous anhydride.		Sodium sulphite.		Water.

$2KHO$	+	SO_2	=	K_2SO_3	+	H_2O
Caustic potash.		Sulphurous anhydride.		Potassium sulphite.		Water.

Tests.—(i) If to a solution of a sulphite some hydrochloric acid be added, sulphurous acid is set free, and this can be readily detected on warming by the evolution of the pungent-smelling sulphur dioxide (*see* tests, p. 192).

(ii) If to sulphurous acid or a solution of a sulphite some zinc and hydrochloric acid are added, the nascent hydrogen will reduce the sulphurous acid to sulphuretted hydrogen (*see* above), which can readily be detected by its odour, and by its blackening a piece of filter-paper moistened with a solution of lead acetate.

SULPHURIC ACID.

Formula, H_2SO_4.

Modes of preparation.—Sulphuric acid is obtained by the oxidation of sulphurous acid. This

Oxidised Sulphurous

may be effected, though very slowly, by exposing sulphurous acid to the air. Sulphuric acid is now manufactured on an enormous scale, the process consisting in oxidising sulphurous acid to sulphuric acid in large leaden chambers, the oxidation being effected in the first place by means of nitric acid, and afterwards by means of nitrogen peroxide produced from the nitric acid and oxygen of the air. The leaden chambers, which are supported by means of external wooden framework, are arranged in a series communicating with one another. Into the first one the flue of a furnace passes; the last one is connected with a tower. Fig. 20 represents the first of the leaden chambers. In the furnace A is burnt sulphur or iron pyrites (FeS_2), the resulting sulphur dioxide passing along with a current of air into the leaden chamber. At the commencement of the process a vessel containing some sodium nitrate and sulphuric

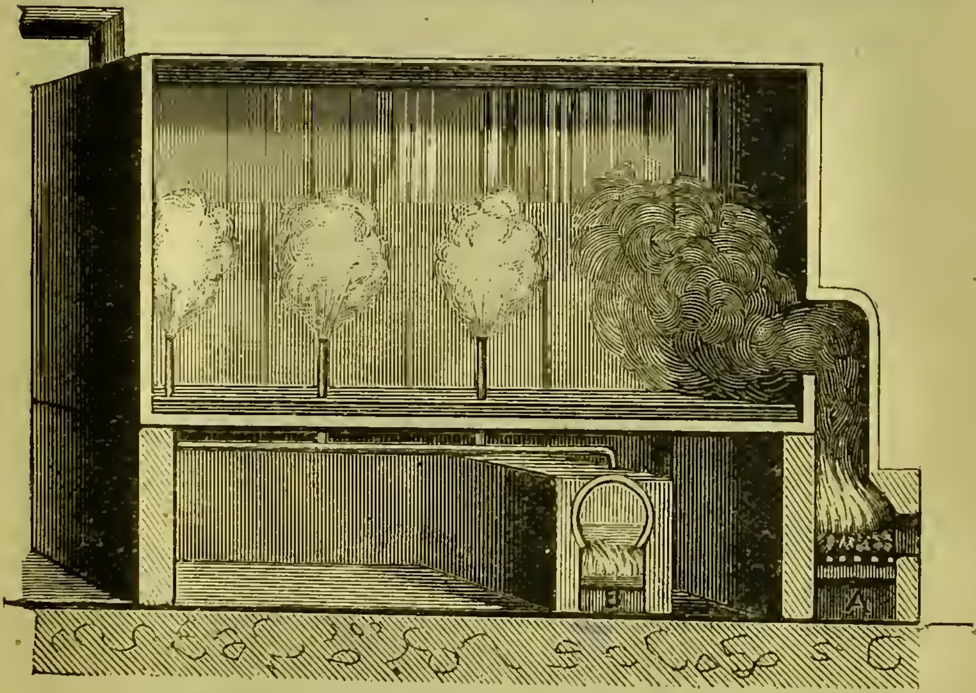


Fig. 20.—Sulphuric Acid Leaden Chamber.

acid is placed within the furnace on one side, so that the vapour of the nitric acid evolved passes with the current of sulphur dioxide and air into the leaden chamber; this vessel only requires re-charging occasionally. The boiler B discharges steam (instead of steam, water spray is often used) into the interior of the chamber, and at the bottom of the chamber the sulphuric acid collects in a diluted condition, and is drawn off from time to time. The formation of the sulphuric acid takes place as follows:—(i) The sulphur dioxide passing into the leaden chamber unites with the steam to form sulphurous acid.

$$\begin{array}{ccccc} SO_2 & + & H_2O & = & H_2SO_3 \\ \text{Sulphur dioxide.} & & \text{Water.} & & \text{Sulphurous acid.} \end{array}$$

(ii) This sulphurous acid is immediately oxidised by the nitric acid vapour to sulphuric acid, nitrogen dioxide being evolved.

$$\begin{array}{ccccccccc} 3H_2SO_3 & + & 2HNO_3 & = & 3H_2SO_4 & + & 2NO & + & H_2O \\ \text{Sulphurous acid.} & & \text{Nitric acid.} & & \text{Sulphuric acid.} & & \text{Nitrogen dioxide.} & & \text{Water.} \end{array}$$

(iii) The nitrogen dioxide then unites with the oxygen of the air that has passed into the chamber to form nitrogen peroxide.

$$\begin{array}{ccccc} 2NO & + & O_2 & = & 2NO_2 \\ \text{Nitrogen dioxide.} & & \text{Oxygen.} & & \text{Nitrogen peroxide.} \end{array}$$

(iv) This nitrogen peroxide oxidises more sulphurous acid to sulphuric acid, nitrogen dioxide being again formed.

$$\begin{array}{ccccccc} 2H_2SO_3 & + & 2NO_2 & = & 2H_2SO_4 & + & 2NO \\ \text{Sulphurous acid.} & & \text{Nitrogen peroxide.} & & \text{Sulphuric acid.} & & \text{Nitrogen dioxide} \end{array}$$

(v) The nitrogen dioxide is again converted by the oxygen of the air into nitrogen peroxide, which then oxidises more sulphurous acid. It will be noticed, therefore, that in this lead-chamber process the oxidation of the sulphurous acid is effected in two different ways: (*a*) by means of nitric acid vapour, a small quantity only of which has to be generated from time to time to start the work of oxidation; (*b*) by means of the nitrogen dioxide, produced by the reduction of the nitric acid, acting as a carrier of the oxygen of the air to the sulphurous acid, by forming nitrogen peroxide, which, oxidising some of the sulphurous acid to sulphuric acid, reproduces nitrogen dioxide, which then carries on its work of combining with the oxygen of the air. The nitrogen dioxide is unable to continue this work for an indefinite period, on account of its being gradually swept away in the current that is passing through the leaden chambers; for, since the air that passes into the chambers contains four-fifths of its bulk of nitrogen, this nitrogen must pass away to make room for the fresh gases and air streaming in. As with this escaping nitrogen a considerable quantity of nitrogen peroxide must pass away, and as this latter gas would very seriously vitiate the atmosphere in the neighbourhood of the sulphuric acid works if allowed to pass into it, some provision has to be made for the absorption of this gas. To effect this, the gases as they escape from the last of the series of leaden chambers are made to pass up a tall tower, known as a Gay-Lussac's tower, in which strong sulphuric acid is kept slowly trickling down over pieces of coke; the nitrogen peroxide is absorbed by the strong sulphuric acid, from which it can be liberated by dilution, and so can be conducted into the first of the leaden chambers, to start its work of oxidation over again. The sulphuric acid that collects at the bottom of the leaden chambers is in a diluted condition, it is known as "chamber acid" and contains about 66 per cent. of H_2SO_4; it is concentrated by evaporation at first in leaden vessels, and afterwards in glass or platinum vessels.

Large quantities of strong sulphuric acid are now made by the direct union of SO_2,O and H_2O with the aid of spongy platinum (*see* page 192).

Properties.—Sulphuric acid, which is commonly known as *oil of vitriol*, is one of the strongest acids; the pure commercial acid is of specific gravity 1·843, and contains 94 per cent. of sulphuric acid. If strong sulphuric acid is mixed with water, the mixture becomes extremely hot, owing to the formation of a molecular compound (H_2SO_4,H_2O). On account of its powerful attraction for water, strong sulphuric acid is employed for the purpose of drying those gases on which it has no chemical action. If sulphuric acid be allowed to drop on hot bricks, or pieces of heated pumice-stone, it is decomposed into water, sulphur dioxide, and oxygen ($2H_2SO_4 = 2H_2O + 2SO_2 + O_2$).

Commercial sulphuric acid is very apt to contain small quantities of lead, arsenic, and nitrogen peroxide as impurities. The lead exists as the sulphate, and is derived from the leaden evaporating vessels in which the acid is concentrated. Although lead sulphate is soluble in strong sulphuric acid, it is not soluble in the dilute acid, and therefore comes down as a white precipitate on diluting the strong acid with water. Arsenic is derived from iron pyrites being used as the source of the sulphur dioxide; arsenic may be detected in the sulphuric acid by diluting it with water, and passing a stream of sulphuretted hydrogen gas through it, when a yellow precipitate of sulphide of arsenic is produced if that impurity is present, or it may be detected by Marsh's test (*see* page 287); sulphuric acid can be manufactured free from arsenic by employing Sicilian sulphur in the place of iron pyrites. Nitrogen

Test for Sulphate.

peroxide is derived from the atmosphere of the leaden chambers; it can be detected by shaking the strong sulphuric acid with powdered ferrous sulphate, which will turn of a dark colour if any nitrogen peroxide be present. Sulphuric acid can be freed from this impurity by boiling with a few crystals of ammonium sulphate, when ammonium nitrite is formed, and immediately decomposed by the heat into nitrogen and water ($NH_4NO_2 = N_2 + 2H_2O$).

Test.—Sulphuric acid, or a soluble sulphate, ~~gives with~~ solution of barium nitrate or chloride a white precipitate, which is insoluble in hydrochloric acid, or, in fact, in any acid.

+ give ppt. $Ba(NO_3)_2$

NORDHAUSEN OR FUMING SULPHURIC ACID.

This is a commercial form of strong sulphuric acid containing sulphuric anhydride in solution, the fumes which it gives off on exposure to the air being caused by the liberation of this sulphuric anhydride. Its composition is usually indicated by the formula $H_2S_2O_7$. It is obtained by first drying crystallised ferrous sulphate ($FeSO_4$, $7H_2O$), which loses six-sevenths of its water, having then the formula $FeSO_4$, H_2O, and then strongly heating this dried ferrous sulphate in clay or earthenware retorts, when the fuming sulphuric acid distils over, ferric oxide (Fe_2O_3) being left in the retort.

H_2S = analogue of H_2O

SULPHURETTED HYDROGEN.

Hydro-
Sulphuric
Sulphide

Formula, H_2S; *liquefies at* $-62°$.

This gas is analogous to water in its composition: the one being an oxide of hydrogen (H_2O), the other a sulphide of hydrogen (H_2S).

Modes of preparation.—(i) This gas is generally prepared for laboratory purposes by the action of sulphuric or hydrochloric acid on sulphide of iron.

FeS	$+$	H_2SO_4	$=$	$FeSO_4$	$+$	H_2S
Ferrous sulphide.		Sulphuric acid.		Ferrous sulphate.		Sulphuretted hydrogen.

Small lumps of sulphide of iron are placed in a bottle (Fig. 21) with two tubulures, C, the bottom of the bottle is covered with broken glass up to the level AA, on this rests the sulphide of iron; dilute sulphuric acid is poured into the bottle B, which is connected with C by a flexible tube: on opening the tap T the acid flows into C, and a brisk evolution of the gas occurs; it is then allowed to pass through some water in a wash-bottle, and thence into whatever solution it is required to be passed. When the tap T is closed the gas accumulates in C and forces the acid up into B, and the evolution of the gas ceases.

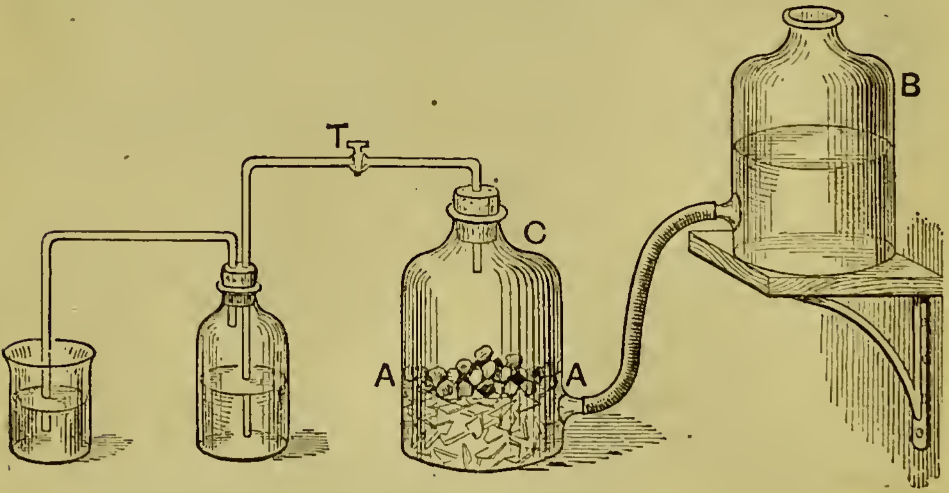


Fig. 21.—Apparatus for making Hydrogen Sulphide.

(ii) It may also be prepared by the action of hydrochloric acid on the native sulphide of antimony.

Sb_2S_3	$+$	$6HCl$	$=$	$2SbCl_3$	$+$	$3H_2S$
Antimony sulphide.		Hydrochloric acid.		Antimony chloride.		Sulphuretted hydrogen.

(iii) Pure sulphuretted hydrogen, such as should be employed in toxicological inquiries, may be obtained by a method suggested by Divers: ordinary H_2S is passed into water containing magnesium hydrate in suspension. The hydrate is converted into hydrosulphide ($Mg(HS)_2$) which dissolves; the clear fluid is poured into a flask furnished with a cork and delivery tube; on warming to 60—65° pure hydrogen sulphide is evolved.

(iv) Another plan is to treat aluminium sulphide with water.

Al_2S_3	$+$	$6H_2O$	$=$	$3H_2S$	$+$	$Al_2(HO)_6$
Aluminium sulphide.		Water.		Hydrogen sulphide.		Aluminium hydrate.

(v) Sulphuretted hydrogen can be obtained in small quantities by direct union of its elements, as when hydrogen is passed over heated sulphur.

Properties.—The specific gravity of sulphuretted hydrogen is 17, and it is somewhat heavier than air; it is a combustible gas, burning with a pale blue flame, and producing sulphur dioxide and water; it is not a supporter of combustion. Sulphuretted hydrogen is a colourless gas, but possesses a peculiar and very disagreeable odour, similar to that of rotten eggs, and a sweetish unpleasant taste. Water at ordinary temperatures dissolves about three times its volume of the gas; but if the solution is kept in a bottle half full of air, the sulphuretted hydrogen is gradually decomposed by the oxygen of the air, sulphur becoming deposited ($2H_2S + O_2 = 2H_2O + S_2$). A little glycerin added to the water tends to preserve the strength of the solution. Sulphuretted hydrogen is a poisonous gas; it can be liquefied by a pressure [illegible] pptd. by H_2S,

of 17 atmospheres at 10°. In a high state of dilution sulphuretted hydrogen is contained in some mineral waters used for medicinal purposes, *e.g.* those of Harrogate and Aix-la-Chapelle; it is also evolved during the putrefactive decomposition of animal matter, eggs, etc.

The slow blackening of oil-paintings is due to the conversion of the white lead of the paint into the black sulphide of lead by slight traces of sulphuretted hydrogen in the air, these traces being derived partly from coal-gas and partly from minute quantities evolved from the human body. If chlorine is brought in contact with sulphuretted hydrogen, the disagreeable smell of the latter immediately disappears, owing to the decomposition of the gas by the chlorine, with liberation of sulphur ($2H_2S + 2Cl_2 = 4HCl + S_2$). As most of the metallic sulphides are insoluble in water, sulphuretted hydrogen precipitates many of the metals from solutions of their salts, and hence is of great use in the separation of many of the metals for analytical purposes. The following equations show the action of sulphuretted hydrogen on some of the metallic salts:—

$HgCl_2$	+	H_2S	=	HgS	+	$2HCl$
Mercuric chloride.		Sulphuretted hydrogen.		Mercuric sulphide.		Hydrochloric acid.
$CuSO_4$	+	H_2S	=	CuS	+	H_2SO_4
Copper sulphate.		Sulphuretted hydrogen.		Copper sulphide.		Sulphuric acid.
$Pb(C_2H_3O_2)_2$	+	H_2S	=	PbS	+	$2HC_2H_3O_2$
Lead acetate.		Sulphuretted hydrogen.		Lead sulphide.		Acetic acid.
$2Bi(NO_3)_3$	+	$3H_2S$	=	Bi_2S_3	+	$6HNO_3$
Bismuth nitrate.		Sulphuretted hydrogen.		Bismuth sulphide		Nitric acid.

[illegible] hydracid H_2S H_2S Na_2S.

$$\underset{\text{Arsenious acid.}}{2H_3AsO_3} + \underset{\text{Sulphuretted hydrogen.}}{3H_2S} = \underset{\text{Arsenious sulphide.}}{As_2S_3} + \underset{\text{Water.}}{6H_2O}$$

Sulphuretted hydrogen is a powerful reducing agent, it reduces ferric salts to ferrous salts, acid solution of potassium bichromate to green chromium salts, etc.; in all such reactions sulphur is precipitated.

Test.—Apart from its odour, which is very characteristic, sulphuretted hydrogen may be detected by its blackening a piece of filter-paper that has been dipped in a solution of lead acetate; the darkening is due to the formation of the black sulphide of lead.

or lead nitrate paper.

HYDROGEN PERSULPHIDE.

Formula, H_2S_2.

This body is analogous to hydrogen peroxide (H_2O_2) in its composition. It may be obtained by pouring a solution of potassium pentasulphide (K_2S_5) into strong hydrochloric acid, when, in addition to the liberation of sulphuretted hydrogen and sulphur, a heavy oily liquid sinks to the bottom, which is the persulphide of hydrogen in a somewhat impure condition. It is a very unstable body, readily decomposing into sulphuretted hydrogen and sulphur.

THIOSULPHURIC ACID.

Hyposulphurous Acid.

Formula, $H_2S_2O_3$.

This acid is not known in the free state, but only in its salts, of which the most important is sodium thiosulphate ($Na_2S_2O_3 + 5H_2O$), commercially known as *hyposulphite of soda.*

Preparation of sodium thiosulphate.—(i) By warming together for some time a solution of sodium sulphite and powdered sulphur.

$$\underset{\text{Sodium sulphite.}}{2Na_2SO_3} + \underset{\text{Sulphur.}}{S_2} = \underset{\text{Sodium thiosulphate.}}{2Na_2S_2O_3}$$

(ii) If sulphur dioxide be passed into calcium sulphide (the alkali-waste obtained in the manufacture of sodium carbonate), it is partly converted into calcium thiosulphate (CaS_2O_3), which by treatment with sodium carbonate yields the soluble sodium thiosulphate and the insoluble calcium carbonate.

$$\underset{\text{Calcium thiosulphate.}}{CaS_2O_3} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} = \underset{\text{Sodium thiosulphate.}}{Na_2S_2O_3} + \underset{\text{Calcium carbonate.}}{CaCO_3}$$

Properties.—Sodium thiosulphate is so named because it is regarded as sodium sulphate (Na_2SO_4) from which one atom of oxygen is withdrawn and an atom of sulphur (θεῖον, sulphur) substituted for it. It is largely employed (under the commercial name of hyposulphite of soda) in photography, on account of the property that it possesses of dissolving the bromide, iodide, and chloride of silver, provided these compounds have not been changed by the action of light; a sensitive photographic plate is covered with a thin layer of one or more of these silver compounds, which becomes decomposed on those parts only on which the light has fallen; after developing the picture, the silver salt that remains unchanged is removed by immersing the plate in a solution of hyposulphite of soda; this is called "fixing" the photograph, it depends upon the formation of a double salt of sodium and silver, $Ag_2Na_4(S_2O_3)_3$, which is soluble in water.

Test.—If to a solution of sodium thiosulphate some hydrochloric acid be added, the smell of sulphur dioxide is evolved, and sulphur is precipitated after the solution has stood for a short time. This reaction is due to the liberation of thiosulphuric acid, which, being extremely unstable, is quickly decomposed into sulphurous acid and sulphur, the former evolving sulphur dioxide, which is known by its odour.

$$\underset{\substack{\text{Sodium}\\\text{thiosulphate.}}}{Na_2S_2O_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Thiosulphuric}\\\text{acid.}}}{H_2S_2O_3} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl}$$

$$\underset{\substack{\text{Thiosulphuric}\\\text{acid.}}}{2H_2S_2O_3} = \underset{\substack{\text{Sulphurous}\\\text{acid.}}}{2H_2SO_3} + \underset{\text{Sulphur.}}{S_2}$$

COMPOUNDS OF SULPHUR AND CHLORINE.

The three following chlorides of sulphur exist; they are all prepared by direct union of sulphur and chlorine:—

S_2Cl_2	Disulphur dichloride.
SCl_2	Sulphur dichloride.
SCl_4	Sulphur tetrachloride.

The first of these is a clear yellow liquid, its vapour attacks the eyes; it is an excellent solvent for sulphur.

$Na_2S_2O_2$

Cl_2.

Part III.

THE METALLIC ELEMENTS AND THEIR PRINCIPAL COMPOUNDS.

CHAPTER I.

CLASSIFICATION OF THE ELEMENTS.

Occurrence of Metals in Nature—General Remarks on the Preparation of Metals and their Compounds.

It has already been noticed that the non-metallic elements seem to arrange themselves in groups or families. Thus, the halogens obviously form a group of closely related elements, and it is found that in such a group there is a more or less regular increase in the atomic weights; thus, the atomic weight of bromine (80) is nearly the mean between the atomic weights of chlorine and iodine $\frac{35 \cdot 5 + 127}{2} = 81 \cdot 2$. In a similar way the elements carbon and silicon, oxygen and sulphur, nitrogen and phosphorus are related. Again, in the metals we have the group lithium, sodium, and potassium; the continuation of the nitrogen family, arsenic, antimony and bismuth, etc.

In 1864 John Newlands pointed out that, if the elements were arranged in the numerical order of their atomic weights, there was a recurrence of similar chemical and physical characters at every eighth element ("The Law of Octaves"); thus (neglecting hydrogen):

Lithium	atomic	weight	7	Sodium	atomic	weight	23
Beryllium	,,	,,	9	Magnesium	,,	,,	24
Boron	,,	,,	11	Aluminium	,,	,,	27
Carbon	,,	,,	12	Silicon	,,	,,	28
Nitrogen	,,	,,	14	Phosphorus	,,	,,	31
Oxygen	,,	,,	16	Sulphur	,,	,,	32
Fluorine	,,	,,	19	Chlorine	,,	,,	35·5

Some five years afterwards this idea was worked out more fully by Mendelejeff, who published a table of the elements arranged according to his "Periodic Law," as represented on p. 208.

The following points should be noticed :—(i) After the first two octaves (lithium to chlorine) the resemblance is most marked between alternate rather than between consecutive octaves ; thus, taking the second vertical column, magnesium, zinc, and cadmium form a natural group, and the other alternate octaves, calcium, strontium, and barium, form a second natural group. (ii) After manganese a triplet of metals occurs, iron, nickel, and cobalt, forming a sort of supplementary eighth vertical column ; the other triplets are ruthenium, rhodium, and palladium, and osmium, iridium, and platinum. The atomic weights in each of these triplets are close together, thus, Fe 56, Co 59, Ni 59. All these metals have high melting points. (iii) The valency of the elements (speaking broadly) may be said to increase as we pass from the first to the seventh column ; thus, sodium is a monad, magnesium a dyad, aluminium a triad, carbon a tetrad, nitrogen a pentad, sulphur a hexad, manganese a heptad ; the same fact is indicated by the formulæ of the oxides at the top of the table. On the other hand, the compounds with hydrogen show a diminishing number of atoms of hydrogen in the molecule as we pass from left to right—thus, CH_4, NH_3, OH_2, ClH.

Besides the great theoretical interest of this

ELEMENTS ARRANGED IN "PERIODS" (NEWLANDS AND MENDELEJEFF).

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
R_2O —	R_2O_2 —	R_2O_3 —	R_2O_4 RH_4	R_2O_5 RH_3	R_2O_6 RH_2	R_2O_7 RH	R_2O_8 (?)
H 1	—	—	—	—	—	—	—
Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
Na 23	24 Mg	27 Al	28 Si	31 P	32 S	35·5 Cl	
K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56. Co 59. Ni 59
63·6 Cu	65·4 Zn	69 Ga	72·5 Ge	75 As	79 Se	80 Br	
Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	—	Ru 102. Rh 103. Pd 106.
108 Ag	112 Cd	113 In	119 Sn	120 Sb	127 Te	127 I	
Cs 133	Ba 137·4	La 138	Ce 140	—	—	—	— — —
—	—	—	—	—	—	—	
—	—	Yb 173	—	Ta 183	W 184	—	Os 191. Ir 193. Pt 195.
197 Au	200 Hg	204 Tl	207 Pb	208 Bi	—	—	
—	—	Th 232	—	—	U 239·5	—	— — —
—	—	—	—	—	—	—	

classification, which is obviously closely connected with some property of the molecules still unknown to us, it is of practical use in several ways.

(i) As a check on the atomic weights; thus, tellurium is an element which closely resembles selenium and sulphur, its old atomic weight was 128, which would place it after iodine in a group to which it was obviously not related; recent determinations have reduced the number to 127, and it seems extremely probable that it has not yet been obtained perfectly pure. Again, the equivalent weight of indium is 38, and its atomic weight was at one time believed to be 38 × 2 = 76, but as there is no space for an element between arsenic and selenium it was suggested that its atomic weight was 38 × 3 = 114, which would place it in the column under aluminium. This number was afterwards confirmed by a determination of its specific heat.

(ii) It enables us to prophesy the existence and properties, physical and chemical, of undiscovered elements; thus, in columns III. and IV., when the table was first published the elements gallium (Ga) and germanium (Ge) were unknown, but by comparing the properties of aluminium and indium in the one case, and of silicon and tin in the other, an accurate forecast of all the chief properties of these elements was made, which was completely verified when the elements were isolated.

There seems to be some difficulty in finding satisfactory places for the recently discovered elements argon, helium, neon, krypton, etc.

A typical **metal** such as silver or iron has the following properties. Its surface, by polishing, acquires what is well known as the metallic lustre; it is a good conductor of heat and electricity, it is opaque to light, very malleable, and its oxide forms a base. Some exceptions to these properties are—

gold-leaf, which allows a greenish light to pass; some metals, as antimony and bismuth, are not malleable, but are very brittle; the higher oxides of some of the metals form acids, as manganic acid (H_2MnO_4), chromic acid (H_2CrO_4), etc. The element arsenic has properties almost exactly half-way between those of a metal and a non-metal. In specific gravity the metals vary from platinum (sp. gr. 21·5) to lithium (sp. gr. 0·59); in fusibility, from platinum melting at 1500°, to mercury, which solidifies at $-38·8°$.

The molecules of zinc, mercury, and cadmium contain but one atom. By Raoult's method of the depression of the freezing point (described in the Organic Part), using melted tin as a solvent, it has been shown that the molecules of nickel, silver, copper, magnesium, lead, bismuth, and calcium are monatomic, while that of aluminium contains two atoms (Al_2).

Some metals—gold, platinum, bismuth, copper, silver—are found native in the earth's crust, but most occur as oxides, sulphides, carbonates, silicates, or chlorides. The first step, in order to obtain the metal from the ore (after purifying the latter by mechanical means, washing, etc.), is to "roast" it—*i.e.* to heat it to a red heat with free access of air. This roasting drives off water, carbon dioxide, arsenic, sulphur, etc., and usually leaves the ore as oxide.

$$\underset{\text{Lead sulphide.}}{PbS} + \underset{\text{Oxygen.}}{3O} = \underset{\text{Lead oxide.}}{PbO} + \underset{\text{Sulphur dioxide.}}{SO_2}$$

The reduction to the metallic state is usually effected by heating with carbon.

$$\underset{\text{Lead oxide}}{PbO} + \underset{\text{Carbon.}}{C} = \underset{\text{Lead.}}{Pb} + \underset{\text{Carbon monoxide.}}{CO}$$

Pr. Mg Ox r Al
using Elect

or cannot

The oxides of two metals cannot be reduced by carbon; these are magnesium oxide and aluminium oxide. In this case either the electric furnace must be used, or the oxide is converted into chloride and the latter decomposed by sodium.

1.
2.

$AlCl_3$	+	$3Na$	=	$3NaCl$	+	Al
Aluminium chloride.		Sodium.		Sodium chloride.		Aluminium.

Oxides can be prepared (i) by heating the metal in air; thus, zinc oxide, tin oxide, magnesium oxide, lead oxide, etc., can be formed. (ii) By heating various salts, when the acid radicle is decomposed and volatilised; thus, by heating barium nitrate, calcium carbonate, aluminium sulphate, the respective oxides will be produced.

Hydrates or hydroxides, when insoluble, are usually obtained by precipitating a solution of a salt with ammonium or potassium hydrate.

Sulphides can be obtained (i) by fusing the metal with sulphur; (ii) by reducing the sulphate of the metal by heating it with carbon; (iii) by passing hydrogen sulphide (H_2S) through a solution of the metal.

1. **Salts.**—In most cases a salt can be prepared by dissolving the carbonate of the metal in the proper acid, filtering or decanting the solution and evaporating to the point of crystallisation; thus, to obtain calcium chloride, dissolve calcium carbonate in hydrochloric acid, decant the clear fluid and evaporate.

2.

$CaCO_3$	+	$2HCl$	=	$CaCl_2$	+	CO_2	+	H_2O
Calcium carbonate.		Hydrochloric acid.		Calcium chloride.		Carbon dioxide.		Water.

The above method fails *when the salt is insoluble*; the salt is then prepared by precipitation; thus, lead sulphate is formed by adding dilute sulphuric acid to graph = [illegible] [illegible] of metals:

a solution of lead nitrate, when the sulphate falls as a white precipitate, which can be filtered off, washed, and dried.

All nitrates and chlorates are soluble in water (bismuth nitrate does not usually give a clear solution).

All chlorides are soluble in water except silver, mercurous, cuprous, and lead chlorides. [illegible]

All sulphates are soluble in water except lead, barium, strontium, and calcium sulphates (the latter is slightly soluble).

Most carbonates and phosphates (except those of sodium, potassium, and ammonium) are insoluble in water.

In the description of the metals which will now be given, the following order of treatment will be adopted with each metal :—(i) A description of the compounds of the metal occurring in nature. (ii) The preparation of the metal from one or more of its natural compounds, together with the physical and chemical properties of the metal. (iii) The preparation of all the important salts of the metal, together with their principal properties. (iv) The analytical tests for the metal.

[illegible]st Strongly Electro positive of all the Elements

POTASSIUM.

Symbol, K ; *monad* ; *atomic weight*, 39.

Natural compounds of potassium. — (i) *Potash felspar* (a double silicate of aluminium and potassium) in granite rocks is the original source of the potassium salts. Plants possess the property of separating and assimilating the potash from rocks and soils, storing it up in their tissues in the form of potassium salts of organic acids (tartrate, citrate, malate, etc.). On burning the wood of plants these

4 Natural Comps } Nitre, Carnallite, Argol, cream of tartar

organic salts are converted by the heat into the carbonate of potassium, which in a somewhat impure condition constitutes *wood-ash* or *pearl-ash*, from which the carbonate of potassium is extracted by water. (ii) *Saltpetre* or *nitre* is native nitrate of potassium (*see* page 116). (iii) *Carnallite* is a double chloride of potassium and magnesium found in Stassfurt, in Germany. (iv) *Argol* is the crude acid tartrate of potassium, or cream of tartar ($KHC_4H_4O_6$), found as a deposit in wine casks. Acid tartrate of potassium is originally present in solution in the juice of the grape; and when this undergoes fermentation in the preparation of wine, the grape sugar becomes converted into alcohol, the latter throwing the acid tartrate of potassium (which is insoluble in alcohol) out of solution. The acid tartrate, carrying down with it some of the colouring matter of the grape, constitutes the deposit known as *argol.*

from melted Caustic potash

Preparation of the metal potassium.—This metal is obtained by distilling potassium carbonate with charcoal, or a mixture of finely divided iron and charcoal with potassium hydrate (Castner's process).

$$\underset{\substack{\text{Potassium}\\ \text{carbonate.}}}{K_2CO_3} + \underset{\text{Charcoal.}}{2C} = \underset{\text{Potassium.}}{2K} + \underset{\substack{\text{Carbon}\\ \text{monoxide.}}}{3CO}$$

Properties of the metal. — Potassium is a
1. metal of a white colour and possesses a bright lustre
2. when a piece of it is freshly cut, the cut surface
3. rapidly tarnishing, however, owing to the action on it of the oxygen of the air, which forms a film of potassium oxide; on account of this strong affinity of potassium for oxygen, the metal has to be kept immersed in mineral naphtha, a liquid free from oxygen, otherwise, if potassium be kept exposed to the

Sp. Gr = ·875.

air, it is soon completely converted into potassium
oxide (K_2O). The specific gravity of potassium is
4. ·875; it therefore floats when thrown on the surface
5. of water; at the same time it energetically decom-
poses the water, forming potassium hydrate, and
6. liberating one-half of the hydrogen. On account of
the violent chemical action, sufficient heat is produced
to ignite this escaping hydrogen, which, from the
presence of a little potassium in it, burns with a
lavender-coloured flame.

$$\underset{\text{Potassium.}}{2K} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Potassium hydrate.}}{2KHO} + \underset{\text{Hydrogen.}}{H_2}$$

On sulphuric and hydrochloric acids potassium acts with explosive violence, forming respectively potassium sulphate and chloride, and liberating the hydrogen. It also forms an explosive compound with carbon monoxide $K_2(CO)_2$.

Potassium hydrate or **caustic potash** (KHO).—Prepared by boiling together potassium carbonate, slaked lime, and water, filtering from the insoluble calcium carbonate produced and evaporating.

$$\underset{\text{Potassium carbonate.}}{K_2CO_3} + \underset{\text{Slaked lime.}}{Ca(HO)_2} = \underset{\text{Potassium hydroxide.}}{2KHO} + \underset{\text{Calcium carbonate.}}{CaCO_3}$$

POTASSIUM SALTS.

Potassium bicarbonate ($KHCO_3$).—Prepared by passing a stream of carbon dioxide through a cold saturated solution of potassium carbonate.

$$\underset{\text{Potassium carbonate.}}{K_2CO_3} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Potassium bicarbonate.}}{2KHCO_3}$$

The potassium bicarbonate being less soluble than the carbonate, crystallises out as it is formed. If boiling water be added to potassium bicarbonate, it is resolved into the carbonate, with evolution of carbon dioxide.

$$\underset{\substack{\text{Potassium}\\\text{bicarbonate.}}}{2KHCO_3} = \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

It should not, on this account, be dissolved in hot water.

$C_2H_3O_2$

Potassium acetate ($KC_2H_3O_2$).—Prepared by neutralising acetic acid with potassium carbonate.

$$\underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2} = \underset{\substack{\text{Potassium}\\\text{acetate.}}}{2KC_2H_3O_2} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

$C_4H_4O_6$

Potassium tartrate ($2K_2C_4H_4O_6 + H_2O$).—Prepared by neutralising potassium acid tartrate (cream of tartar), dissolved in boiling water, with potassium carbonate.

$$\underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} + \underset{\substack{\text{Potassium}\\\text{acid tartrate.}}}{2KHC_4H_4O_6} = \underset{\substack{\text{Potassium}\\\text{tartrate.}}}{2K_2C_4H_4O_6} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

$C_6H_5O_7$

Potassium citrate ($K_3C_6H_5O_7 + H_2O$).—Prepared by neutralising a solution of citric acid with potassium carbonate.

$$\underset{\substack{\text{Potassium}\\\text{carbonate.}}}{3K_2CO_3} + \underset{\text{Citric acid.}}{2H_3C_6H_5O_7} = \underset{\substack{\text{Potassium}\\\text{citrate.}}}{2K_3C_6H_5O_7} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{3CO_2} + \underset{\text{Water.}}{3H_2O}$$

Potassium citrate is also prepared by the action of citric acid on potassium bicarbonate.

Potassium sulphate (K_2SO_4).—Prepared by neutralising sulphuric acid with potassium carbonate.

$$\underset{\text{Potassium carbonate.}}{K_2CO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Potassium sulphate.}}{K_2SO_4} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Also obtained as a bye-product in the preparation of nitric acid from potassium nitrate and sulphuric acid.

$$\underset{\text{Potassium nitrate.}}{2KNO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Potassium sulphate.}}{K_2SO_4} + \underset{\text{Nitric acid.}}{2HNO_3}$$

Potassium nitrate (KNO_3).—Found in nature as *nitre* or *saltpetre*. It may be prepared by neutralising nitric acid with potassium carbonate. This salt is largely employed in the manufacture of gunpowder, which is a mixture of charcoal, sulphur, and nitre; when the gunpowder is fired, the oxygen of the nitre converts the charcoal into the two gaseous oxides of carbon, carbon monoxide and dioxide, the nitrogen of the nitre is set free, and the sulphur unites with the potassium of the nitre to form potassium sulphide, which, blown into the air in minute particles, constitutes the smoke. This may be roughly represented by the equation :

$$\underset{\text{Nitre.}}{2KNO_3} + \underset{\text{Sulphur.}}{S} + \underset{\text{Charcoal.}}{3C} = \underset{\text{Potassium sulphide.}}{K_2S} + \underset{\text{Nitrogen.}}{2N} + \underset{\text{Carbon dioxide.}}{3CO_2}$$

The explosive violence is due to the sudden expansion of the large volume of the heated gases

[illegible] : C 15 = 10
S 10

produced. The temperature produced is very high—2200°.

Potassium nitrite (KNO_2).—If potassium nitrate be heated to redness for some time, it loses one-third of its oxygen, and potassium nitrite is formed.

Potassium chloride (KCl) occurs in nature as *carnallite*; it can be prepared by neutralising hydrochloric acid with potassium carbonate.

Potassium iodide (KI).—This important salt is prepared (i) by saturating a hot solution of caustic potash with iodine, by which means potassium iodide and iodate are obtained in solution.

$$\underset{\substack{\text{Potassium}\\\text{hydrate.}}}{6KHO} + \underset{\text{Iodine.}}{3I_2} = \underset{\substack{\text{Potassium}\\\text{iodide.}}}{5KI} + \underset{\substack{\text{Potassium}\\\text{iodate.}}}{KIO_3} + \underset{\text{Water.}}{3H_2O}$$

(ii) The solution is then evaporated to dryness, and the residue mixed with charcoal and heated, so as to convert the iodate into iodide; the carbon abstracting the oxygen from the iodate, and so reducing it to the iodide.

$$\underset{\substack{\text{Potassium}\\\text{iodate.}}}{2KIO_3} + \underset{\text{Carbon.}}{6C} = \underset{\substack{\text{Potassium}\\\text{iodide.}}}{2KI} + \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{6CO}$$

(iii) The melted mass on cooling is boiled with water, the solution of potassium iodide is filtered from excess of charcoal, evaporated to a low bulk, and set aside to crystallise. It is very important that the iodate of potassium should be completely converted into iodide, as any acid possesses the property of liberating iodine from a mixture of the two salts; and since iodide of potassium is frequently administered in medicine in very large doses, if it contained iodate the hydrochloric acid of the gastric juice would liberate iodine from the two salts within the stomach, and so the iodine might be set free in poisonous quantities. The hydrochloric acid of the gastric juice would first liberate from the iodide and iodate hydriodic and iodic acids respectively.

$$\underset{\substack{\text{Potassium}\\\text{iodide.}}}{5KI} + \underset{\substack{\text{Potassium}\\\text{iodate.}}}{KIO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6HCl} = \underset{\substack{\text{Hydriodic}\\\text{acid.}}}{5HI} + \underset{\substack{\text{Iodic}\\\text{acid.}}}{HIO_3} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{6KCl}$$

These two acids would then by their action on one another produce free iodine and water.

$$\underset{\substack{\text{Hydriodic}\\\text{acid.}}}{5HI} + \underset{\substack{\text{Iodic}\\\text{acid.}}}{HIO_3} = \underset{\text{Iodine.}}{3I_2} + \underset{\text{Water.}}{3H_2O}$$

Potassium bromide (KBr).—This salt is prepared in a similar manner to the iodide, with the substitution of bromine for iodine.

Potassium manganate (K_2MnO_4).—Prepared by fusing together in a crucible caustic potash, potassium chlorate and manganese dioxide, and extracting the mass with *cold* water, when a green-coloured solution of potassium manganate is obtained.

$$\underset{\substack{\text{Potassium}\\\text{hydrate.}}}{6KHO} + \underset{\substack{\text{Potassium}\\\text{chlorate.}}}{KClO_3} + \underset{\substack{\text{Manganese}\\\text{dioxide.}}}{3MnO_2} = \underset{\substack{\text{Potassium}\\\text{manganate.}}}{3K_2MnO_4} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{KCl} + \underset{\text{Water.}}{3H_2O}$$

On the large scale the chlorate of potash is omitted, and the oxygen obtained directly from the air.

$$\underset{\substack{\text{Manganese}\\\text{dioxide.}}}{MnO_2} + \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{2KHO} + \underset{\text{Oxygen.}}{O} = \underset{\substack{\text{Potassium}\\\text{manganate.}}}{K_2MnO_4} + \underset{\text{Water}}{H_2O}$$

This solution of potassium manganate is used as a disinfectant under the name of *Condy's green fluid;* it acts partly as a germicide, and partly by the readiness with which it oxidises organic substances. It is not employed so much as the permanganate, which is a better and more powerful disinfectant.

Potassium permanganate ($KMnO_4$).—This salt is also known as the *red manganate of potash*, and as a disinfectant is largely used under the name of *Condy's red fluid.* It is obtained from the manganate by the abstraction of one-half of the potassium, which can be effected either by boiling the solution of the green manganate, or by passing a stream of carbon dioxide or chlorine through it. One-half of the potassium is removed respectively as potassium hydrate, carbonate or chloride, some manganese dioxide being precipitated.

$$\underset{\text{Potassium manganate.}}{3K_2MnO_4} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Potassium permanganate.}}{2KMnO_4} + \underset{\text{Potassium hydrate.}}{4KHO} + \underset{\text{Manganese dioxide.}}{MnO_2}$$

$$\underset{\text{Potassium manganate.}}{3K_2MnO_4} + \underset{\text{Carbon dioxide.}}{2CO_2} = \underset{\text{Potassium permanganate.}}{2KMnO_4} + \underset{\text{Potassium carbonate.}}{2K_2CO_3} + \underset{\text{Manganese dioxide.}}{MnO_2}$$

By evaporating the deep red solution to a low bulk and allowing it to cool, potassium permanganate separates in long, dark-red, almost black, needles, with somewhat of a metallic lustre. Potassium permanganate is one of the most powerful oxidising agents known, and is also a powerful disinfectant; as a disinfectant it acts in a similar manner to the manganate, partly by being a powerful germicide, and partly by the readiness with which it oxidises organic substances; when it is being so employed, the red solution loses its colour, a brown deposit of manganese dioxide being produced; the splitting up of potassium permanganate when employed as a disinfectant is shown in the following equation:—

$$\underset{\text{Potassium permanganate.}}{4KMnO_4} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Manganese dioxide.}}{4MnO_2} + \underset{\text{Potassium hydrate.}}{4KHO} + \underset{\text{Oxygen.}}{3O_2}$$

On account of the staining that would result from the deposition of the manganese dioxide, a solution of potassium permanganate should never be employed in the disinfection of linen or of articles of clothing.

Sulphurated potash.—This preparation, which is a mixture of potassium pentasulphide (K_2S_5) and potassium sulphate (K_2SO_4), is obtained by fusing together potassium carbonate and sulphur. It is an unstable preparation and was formerly known as *liver of sulphur.*

Potassium chlorate. (*See* page 140.)

Potassium cyanide, cyanate, ferrocyanide, and ferricyanide.—These salts will be described in the Organic Chemistry Section, Chapter III.

Tests for Potassium.

(i) If a potassium salt, or a solution of a potassium salt, be introduced on a loop of platinum wire into a Bunsen flame, a characteristic lavender tint will be imparted to the flame. If a sodium salt be also present, the yellow colour imparted by the sodium to

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the flame will entirely mask the lavender tint produced by the potassium salt; but if such a flame be viewed through a piece of dark-blue glass, the yellow sodium rays will be absorbed by the blue of the glass, while the lavender-coloured rays produced by the potassium salt will pass through the glass unchanged.

(ii) If a solution of a potassium salt contained in a watch-glass be acidulated with hydrochloric acid, a few drops of platinic chloride added, and the mixture well stirred with a glass rod, a yellow crystalline deposit of the double platinum and potassium chloride ($PtCl_4,2KCl$) will be formed. A similar reaction is also produced with ammonium salts.

(iii) If to a concentrated solution of a potassium salt a strong solution of tartaric acid be added, and the mixture then be well shaken or stirred, a white granular or crystalline precipitate of potassium acid tartrate ($KHC_4H_4O_6$) will be formed.

Cream of tartar.

CHAPTER II.

SODIUM—LITHIUM.

Sodium—Natural Compounds of Sodium—Preparation and Properties of the Metal Sodium—Preparation of the Sodium Salts—Leblanc process—Ammonia-Soda process—Test for Sodium—Lithium—Natural Compounds of Lithium—Preparation and Properties of the Metal Lithium—Preparation of the Lithium Salts—Test for Lithium.

SODIUM.

Symbol, Na ; *monad ; atomic weight*, 23.

Natural compounds of sodium.—(i) Sodium chloride is the principal sodium compound occurring in nature ; in the solid form it occurs as *common salt*, or *rock-salt ;* in solution it is present in large quantities in sea-water. (ii) Sodium nitrate, known as *cubic nitre* or *Chili saltpetre*, occurs in immense quantities in South America. (iii) Just as potassium salts are present in land plants, and leave the carbonate when the plants are burnt, so sodium salts are present in sea-weeds, and are left as sodium carbonate when sea-weeds are burnt (*see* page 147). (iv) *Cryolite* is a double aluminium and sodium fluoride ($AlF_3,3NaF$).

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Preparation of the metal sodium.—This metal is prepared by a process similar to that employed in the preparation of potassium, viz. by distilling sodium carbonate with charcoal, or a mixture of finely-divided iron and charcoal with sodium hydrate.

$$\underset{\text{Sodium carbonate.}}{\boxed{Na_2CO_3}} + \underset{\text{Carbon.}}{2C} = \underset{\text{Sodium.}}{2Na} + \underset{\text{Carbon monoxide.}}{3CO}$$

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2 · Electrolysis of molten hydrox. @ 300°

Most of the metallic sodium at the present time is obtained by decomposing, by means of a powerful 2 current of electricity, melted sodium hydrate at a temperature of 300°, nickel electrodes being used.

Properties of the metal.—Sodium very much resembles potassium in many of its properties. It is a metal of a silver-white colour and possesses a bright lustre when freshly cut, the cut surface rapidly tarnishing, however, owing to its uniting with the oxygen of the air to form a film of sodium oxide; it is on account of this powerful affinity of sodium for oxygen that the metal has to be kept immersed in mineral naphtha, a liquid free from oxygen; as otherwise, if kept exposed to the air, it would become completely converted into sodium oxide (Na_2O). Sodium has a specific gravity of ·973, and therefore floats when thrown on water, at the same time decomposing the water energetically, forming sodium hydrate, and liberating one-half of the hydrogen of the water.

$$\underset{\text{Sodium.}}{2Na} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Sodium}\\\text{hydrate.}}}{2NaHO} + \underset{\text{Hydrogen.}}{H_2}$$

There is not as much heat generated by the action of sodium on water as by potassium on water, and therefore during the action of sodium on water the escaping hydrogen is not ignited; but if the movements of the sodium on the surface of the water be restrained, as, for instance, by throwing a piece of sodium on to wet blotting-paper, when it remains fixed in one spot, then the heat, being concentrated at this one spot, is sufficiently intense to ignite the escaping hydrogen. Large quantities of sodium are used for preparing sodium cyanide (for extracting gold) and sodium peroxide (used for bleaching).

Sodium oxide (Na_2O).—Prepared by heating sodium to 180° in the air; it forms a grey solid.

Sodium peroxide (Na_2O_2).—Prepared by heating sodium to 300° in excess of air; it is a white solid and a most powerful oxidising agent. When dissolved in hydrochloric acid it forms a solution of salt and peroxide of hydrogen, which is much used for bleaching straw, etc.

Sodium hydrate or **hydroxide** (caustic soda).—Prepared by boiling a solution of sodium carbonate with solid slaked lime until the clear liquid ceases to effervesce; the liquid is then evaporated till the hydrate begins to volatilise, when it is poured into moulds and cast into sticks. The reaction should be performed in an iron or silver dish. The equation is quite similar to that given under potassium hydrate.

$Na_2CO_3 + Ca(HO)_2 = 2NaOH + CaCO_3$

SODIUM SALTS.

Sodium carbonate (Na_2CO_3).—Washing soda ($Na_2CO_3 + 10H_2O$).—The latter substance is manufactured on an enormous scale from common salt (NaCl). There are two methods of manufacturing sodium carbonate on a large scale, one known as the *Leblanc process*, the other and more recent one as the *ammonia-soda process*.

Leblanc process.—In this process the sodium is furnished by common salt (NaCl), and the carbonic radicle by chalk or limestone ($CaCO_3$). The roasting of these two substances together would be useless, since even if sodium carbonate and calcium chloride were formed, yet they could not be separated from one another, for both being soluble in water they would, on the addition of water, react on one another, reproducing sodium chloride and calcium carbonate. The object of the process is therefore to finally obtain an insoluble calcium compound from which the sodium carbonate may be removed by solution in water. This is effected by the following steps:—

(i) The sodium chloride is converted into sodium sulphate by the action of strong sulphuric acid.

$$\underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl}$$

(ii) The sodium sulphate (*salt-cake*) is then mixed with small coal and crushed limestone, and the mixture thoroughly heated in a furnace; the sodium sulphate is first reduced by the carbon of the coal to sodium sulphide.

$$\underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4} + \underset{\text{Carbon.}}{4C} = \underset{\substack{\text{Sodium}\\\text{sulphide.}}}{Na_2S} + \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{4CO}$$

Double decomposition then takes place between the sodium sulphide and the calcium carbonate (limestone), resulting in the formation of sodium carbonate and calcium sulphide.

$$\underset{\substack{\text{Sodium}\\\text{sulphide.}}}{Na_2S} + \underset{\substack{\text{Calcium}\\\text{carbonate.}}}{CaCO_3} = \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Calcium}\\\text{sulphide.}}}{CaS}$$

(iii) The melted mass (*black-ash*) is boiled with water in order to dissolve out the sodium carbonate, the calcium sulphide remaining insoluble; the latter is allowed to deposit; the solution of sodium carbonate is poured off and evaporated until it crystallises on cooling.

Ammonia-soda process (Solvay's process). This consists in passing carbon dioxide into an ammoniacal solution of salt under a pressure of two atmospheres.

$$\underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Salt.}}{NaCl} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sodium}\\\text{bicarbonate.}}}{HNaCO_3} + \underset{\substack{\text{Ammonium}\\\text{chloride.}}}{NH_4Cl}$$

The bicarbonate being less soluble than the salt separates out as it forms; it is filtered off and dried by steam, when it is converted into sodium carbonate.

$$\underset{\substack{\text{Sodium}\\\text{bicarbonate.}}}{2NaHCO_3} = \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

The carbon dioxide gas which is given off is again used, and the ammonia is recovered from the ammonium chloride by heating with lime.

Sodium carbonate, commonly known as *washing-soda,* is largely used to soften water for washing purposes; the water is usually first boiled, by which means the temporary hardness is got rid of (*see* page 88), and some washing-soda is then added to get rid of the permanent hardness, which is mainly due to calcium and magnesium sulphates; these compounds are converted into the insoluble calcium and magnesium carbonates by the washing-soda.

Sodium bicarbonate ($NaHCO_3$) is prepared by passing a stream of carbon dioxide through a saturated solution of sodium carbonate, when the bicarbonate separates out, on account of its lesser solubility.

$$\underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sodium}\\\text{bicarbonate.}}}{2NaHCO_3}$$

Sodium bicarbonate, when employed in medicine, should not be dissolved in hot water, as it is converted by the heat into sodium carbonate.

$$\underset{\substack{\text{Sodium}\\\text{bicarbonate.}}}{2NaHCO_3} = \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Sodium sulphate ($Na_2SO_4 + 10H_2O$).—This salt, a saline purgative, is known as *Glauber's salt.*

H H H } PO_4 H H } PO_4 Na H } PO_4 Na Na } PO_4

It is prepared either by neutralising sulphuric acid with sodium carbonate, or as a by-product in the preparation of hydrochloric acid from common salt and sulphuric acid.

$$\underset{\text{Sodium carbonate.}}{Na_2CO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon dioxide.}}{CO_2}$$

$$\underset{\text{Sodium chloride.}}{2NaCl} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Hydrochloric acid.}}{2HCl}$$

Sodium phosphate ($Na_2HPO_4 + 12H_2O$) is prepared by partially saturating phosphoric acid with caustic soda. This salt, although an acid phosphate in constitution, is yet alkaline to test-paper. Another sodium phosphate (NaH_2PO_4), which can be prepared by only one-third neutralising phosphoric acid with caustic soda, is acid to test-paper.

Sodium ammonium hydrogen phosphate or **microcosmic salt** ($NaNH_4HPO_4 + 4H_2O$) is prepared by mixing boiling solutions of sodium phosphate and ammonium chloride.

PO_4

$$\underset{\text{Sodium phosphate.}}{Na_2HPO_4} + \underset{\text{Ammonium chloride.}}{NH_4Cl} = \underset{\text{Microcosmic salt.}}{NaNH_4HPO_4} + \underset{\text{Sodium chloride.}}{NaCl}$$

It is used in blowpipe tests, as it yields, when heated, a transparent bead of sodium metaphosphate.

$$\underset{\text{Microcosmic salt.}}{NaNH_4HPO_4} = \underset{\text{Sodium metaphosphate.}}{NaPO_3} + \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Water.}}{H_2O}$$

Sodium arseniate (Na_2HAsO_4) is prepared by fusing together arsenious oxide (white arsenic), sodium carbonate, and sodium nitrate, and dissolving the mass in water.

$$\underset{\text{Arsenious oxide.}}{As_2O_3} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} + \underset{\text{Sodium nitrate.}}{2NaNO_3} =$$

$$\underset{\text{Sodium pyroarseniate.}}{Na_4As_2O_7} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Nitrogen trioxide.}}{N_2O_3}$$

$$\underset{\text{Sodium pyroarseniate.}}{Na_4As_2O_7} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sodium arseniate.}}{2Na_2HAsO_4}$$

Sodium hypophosphite ($NaPH_2O_2 + H_2O$) is prepared either by boiling phosphorus with solution of caustic soda (*see* page 181), or by decomposing a solution of calcium hypophosphite with sodium carbonate, when calcium carbonate is precipitated and sodium hypophosphite remains in solution.

$$\underset{\text{Calcium hypophosphite.}}{Ca(PH_2O_2)_2} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} = \underset{\text{Sodium hypophosphite.}}{2NaPH_2O_2} + \underset{\text{Calcium carbonate.}}{CaCO_3}$$

Sodium iodide (NaI) and **sodium bromide** ($NaBr$).—These salts are prepared in similar ways to the corresponding potassium salts, substituting caustic soda for caustic potash (*see* pages 217, 218).

Sodium acetate ($NaC_2H_3O_2$) is prepared by neutralising acetic acid with sodium carbonate.

$$\underset{\text{Acetic acid.}}{2HC_2H_3O_2} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} = \underset{\text{Sodium acetate.}}{2NaC_2H_3O_2} +$$

$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Sodium potassium tartrate ($KNaC_4H_4O_6 + 4H_2O$).—This salt, which is largely used as a saline purgative, is known as *Rochelle salt*; it is prepared by neutralising a hot solution of potassium acid tartrate (cream of tartar) with sodium carbonate.

$$\underset{\text{Potassium acid tartrate.}}{2KHC_4H_4O_6} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} = \underset{\text{Sodium potassium tartrate.}}{2KNaC_4H_4O_6} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

This salt constitutes the main ingredient of a *Seidlitz powder*, the blue packet of which contains a mixture of Rochelle salt and sodium bicarbonate, whilst the white packet contains tartaric acid; the contents of the blue packet are first dissolved in water, and then the contents of the white packet added; the sodium bicarbonate is neutralised by the tartaric acid, with formation of sodium tartrate and copious effervescence of carbon dioxide gas.

$$\underset{\text{Sodium bicarbonate.}}{2NaHCO_3} + \underset{\text{Tartaric acid.}}{H_2C_4H_4O_6} = \underset{\text{Sodium tartrate.}}{Na_2C_4H_4O_6} + \underset{\text{Carbon dioxide.}}{2CO_2} + \underset{\text{Water.}}{2H_2O}$$

But as the white packet contains a slight excess of tartaric acid over and above what is required to neutralise the bicarbonate, this slight excess of acid will convert a small portion of the sodium tartrate into the acid tartrate, which will then give an agreeable acidity to the draught.

$$\underset{\text{Sodium tartrate.}}{Na_2C_4H_4O_6} + \underset{\text{Tartaric acid.}}{H_2C_4H_4O_6} = \underset{\text{Sodium acid tartrate.}}{2NaHC_4H_4O_6}$$

So that when the contents of the two packets constituting the "seidlitz powder" are mixed in water, three salts, all of them saline purgatives, are contained in the draught, viz. sodium potassium tartrate (Rochelle salt), sodium tartrate, and sodium acid tartrate.

Sodium citro-tartrate.—This effervescing preparation, known as the *effervescing citro-tartrate of soda*, is prepared by mixing together in the solid state, sodium bicarbonate, citric acid, tartaric acid, and sugar, and then carefully heating the mass until it becomes granular. When the granules are dissolved in water, effervescence takes place, with the production of sodium citro-tartrate.

Sodium hypochlorite. (*See* page 139.)

Sodium thiosulphate or **hyposulphite.** (*See* page 203.)

Sodium borate. (*See* page 170.)

Test for Sodium.

Group VI.

If a fragment of a sodium salt, or some solution of a sodium salt, be introduced, on a loop of platinum wire, into a Bunsen flame, an intense yellow colour will be communicated to the flame; this test will be rendered all the more trustworthy by observing the effect of the yellow-coloured sodium flame upon the skin of the hand when held near the flame, the skin then appearing of a ghastly livid colour.

LITHIUM.

Symbol, Li; *monad; atomic weight*, 7.

Natural compounds of lithium.—Lithium occurs in the minerals *lepidolite* and *petalite*, and is also found in minute quantities in numerous mineral springs.

Electrolysis
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Preparation and properties of the metal lithium.—Lithium can be prepared by electrolysis of its fused chloride; the metal depositing on the negative pole and chlorine being liberated at the positive pole. Lithium is the lightest solid known (specific gravity, ·59); it is a silver-white metal, harder than potassium or sodium, but oxidising less easily than those metals; its cut surface, however, soon tarnishes from absorption of oxygen and formation of lithium oxide, it is therefore kept in mineral naphtha. Like potassium and sodium, it decomposes water when thrown upon it, with the formation of lithium hydrate and hydrogen, but the escaping hydrogen is not inflamed.

LITHIUM SALTS.

Lithium carbonate (Li_2CO_3) is prepared from *lepidolite*, a double fluoride of potassium and lithium with silicate of aluminium, by decomposing it with sulphuric acid to form the three soluble sulphates of potassium, lithium, and aluminium, adding ammonia to precipitate the aluminium, filtering, evaporating to dryness, igniting the residue to expel ammonium salts, dissolving the potassium and lithium sulphates in a small quantity of water, and adding potassium carbonate to precipitate the carbonate of lithium.

Lithium bicarbonate ($LiHCO_3$) is prepared by suspending lithium carbonate in water, and passing carbon dioxide gas, when the bicarbonate is formed and dissolves in the water.

$$\underset{\substack{\text{Lithium}\\\text{carbonate.}}}{Li_2CO_3} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Lithium}\\\text{bicarbonate.}}}{2LiHCO_3}$$

This is the salt that is present in lithia water (*Liquor lithiæ effervescens*).

Lithium citrate ($Li_3C_6H_5O_7$) is prepared by neutralising a solution of citric acid with lithium carbonate.

$$\underset{\text{Lithium carbonate.}}{3Li_2CO_3} + \underset{\text{Citric acid.}}{2H_3C_6H_5O_7} = \underset{\text{Lithium citrate.}}{2Li_3C_6H_5O_7} + \underset{\text{Carbon dioxide.}}{3CO_2} + \underset{\text{Water.}}{3H_2O}$$

ul test.

Test for Lithium.

Lithium salts impart a magnificent crimson colour to the Bunsen flame, ~~when introduced into the flame~~ on a loop of platinum wire; the colour is ~~rendered~~ more intense by previously moistening ~~the wire with~~ hydrochloric acid, so as to form lithium chloride.

CHAPTER III.

CALCIUM—BARIUM—STRONTIUM.

Calcium—Natural Compounds of Calcium—Preparation of the Calcium Salts—Mortars and Cements—Tests for Calcium—Barium—Natural Compounds of Barium—Preparation of the Barium Salts—Tests for Barium—Strontium.

CALCIUM.

Symbol, Ca; *dyad; atomic weight*, 40; *specific gravity*, 1·85.

Natural compounds of calcium—(i) The chief calcium compound found in nature is the carbonate, which occurs in a variety of forms; in a pure crystalline form it occurs as *Iceland spar* and *calc spar;* in less pure forms it constitutes *marble*, *chalk*, *limestone*, *oolite*, and *coral;* the shells of mollusca and the egg-shells of birds consist mainly of calcium carbonate; *stalactites* consist of a porous form of calcium carbonate, produced by the evaporation of hard water containing the calcium bicarbonate in solution; they are found hanging from the roofs of limestone caves. (ii) Calcium sulphate occurs in nature as *alabaster*, used as an ornamental stone; as *selenite*, which is found in transparent plates, and is used for optical purposes; and as *gypsum*, a form of calcium sulphate containing water of crystallisation ($CaSO_4,2H_2O$). By heating gypsum for some time at 130° to 140° the water of crystallisation is partly expelled, and commercial *plaster of Paris* is obtained; this, if mixed with sufficient water to form a paste, sets to a solid in a short time, due to the plaster of Paris ($CaSO_4$) uniting with the water to form gypsum ($CaSO_4, 2H_2O$), a body in which the water is in the solid state. Plaster of Paris is largely employed in this way as a cement, and by the surgeon to form a rigid casing for fractured limbs, etc. (iii) Calcium fluoride is native *fluor-spar.* (iv) Calcium phosphate is the principal constituent of the minerals *apatite* and *phosphorite.* (v) Calcium silicate is a constituent of many rocks.

Preparation and properties of the metal calcium.—This is a rare metal; it may be prepared by the electrolysis of fused calcium iodide, the calcium being deposited upon the negative pole. Moissan has recently obtained it pure by crystallising the metal from sodium, and then dissolving the sodium by alcohol; it is a white metal, melting at 76°, rather harder than lead; it decomposes water.

Calcium oxide or **lime** (CaO) is prepared by heating limestone (calcium carbonate) until all the carbon dioxide is expelled.

$$\underset{\text{Calcium carbonate.}}{CaCO_3} = \underset{\text{Lime.}}{CaO} + \underset{\text{Carbon dioxide.}}{CO_2}$$

The manufacture of lime, or quicklime as it is commonly called, is carried on in specially constructed furnaces called *lime-kilns.* Fig. 22 represents such a kiln, which is constructed of fire-bricks, and is filled with pieces of limestone (A). A fire is kept up at the side (B), and the lime is raked out from the bottom of the kiln (C) as it is produced, fresh limestone being introduced at the top to supply its place.

Calcium hydrate or **slaked lime** ($Ca(HO)_2$) is prepared by the addition of water to lumps of quicklime, when considerable heat is produced, due partly to the chemical action taking place between the quicklime and the water, and partly to the conversion of the latent heat of the water into sensible heat, as the water passes from the liquid state into the solid state in which it exists in calcium hydrate

$$\underset{\text{Quicklime.}}{CaO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Slaked lime.}}{Ca(HO)_2}$$

Lime-water (*Liquor calcis*, B. P.) is a saturated solution of slaked lime in water, each pint containing about 13 grains of calcium hydrate in solution; calcium hydrate is much more soluble in an aqueous solution of sugar, and such a solution is the *saccharated lime water* (*Liquor calcis saccharatus*, B. P.), which contains about 14 times as much slaked lime as ordinary lime-water. If lime-water be exposed to the air it soon diminishes in strength, owing to the absorption of carbon dioxide from the air, and consequent precipitation of calcium carbonate.

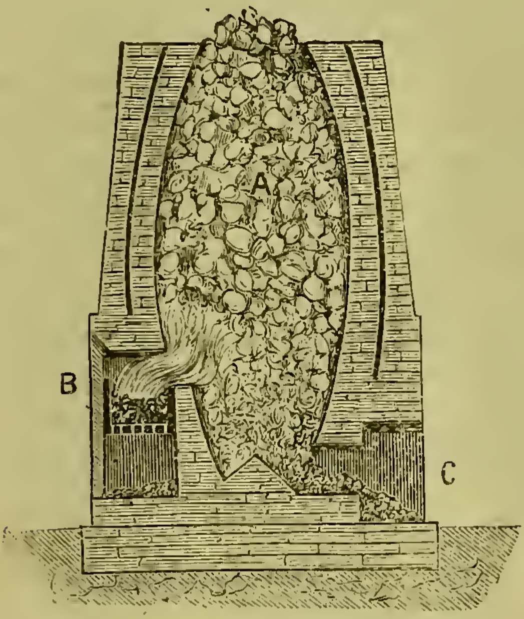


Fig. 22.—Section of Lime-Kiln.

Slaked lime is largely employed in the preparation of *mortar*, which consists of slaked lime, sand, and water mixed so as to form a paste; the "setting" of ordinary mortar is due to a slow combination of the carbon dioxide with the slaked lime.

$$\underset{\text{Slaked lime.}}{Ca(HO)_2} + \underset{\text{Carbon dioxide.}}{CO_2} = \underset{\text{Calcium carbonate.}}{CaCO_3} + \underset{\text{Water.}}{H_2O}$$

It will be noticed that water is evolved in this reaction, this accounts for the persistent dampness of newly-built houses in which mortar is "setting." *Hydraulic mortars* or *cements* are preparations which, when mixed with water, solidify, and then continue to harden under water, until they assume a stone-like hardness; such are *Roman cement* and *Portland cement*, which are obtained by calcining a mixture of limestone and clay; on mixing the cement with water, compounds of lime, alumina, and silica are produced in addition to the calcium carbonate, which set to a hard mass impervious to water. *Concrete* consists of hydraulic cement mixed with gravel or crushed pebbles.

CALCIUM SALTS.

Calcium chloride ($CaCl_2 + 6H_2O$) is prepared by dissolving chalk or marble (calcium carbonate) in hydrochloric acid and evaporating the solution.

$$\underset{\text{Calcium carbonate.}}{CaCO_3} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Calcium chloride.}}{CaCl_2} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Calcium chloride, when heated to 200°, loses 4 molecules of water of crystallisation, forming a porous mass known as "fused chloride of calcium." This is one of the most hygroscopic bodies known; if exposed to the air for a short time it becomes liquid, owing to its absorbing sufficient water from the air to dissolve in; on account of its hygroscopic properties it is frequently employed to dry gases.

Calcium carbonate ($CaCO_3$).—This compound, as previously mentioned, occurs native in several forms. As *precipitated carbonate of lime*, it is prepared by precipitating a solution of calcium chloride with a solution of sodium carbonate.

$$\underset{\substack{\text{Calcium}\\ \text{chloride.}}}{CaCl_2} + \underset{\substack{\text{Sodium}\\ \text{carbonate.}}}{Na_2CO_3} = \underset{\substack{\text{Calcium}\\ \text{carbonate.}}}{CaCO_3} + \underset{\substack{\text{Sodium}\\ \text{chloride.}}}{2NaCl}$$

Prepared chalk is merely washed chalk that has been worked into small conical lumps and then dried; if washed chalk be made into larger rolls it constitutes *whiting*.

Calcium phosphate ($Ca_3(PO_4)_2$) is prepared by digesting bone-ash (impure calcium phosphate) in hydrochloric acid, by which means the insoluble calcium phosphate is converted into the soluble calcium superphosphate or acid phosphate and calcium chloride.

$$\underset{\substack{\text{Calcium}\\ \text{phosphate.}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{4HCl} = \underset{\substack{\text{Calcium}\\ \text{acid phosphate.}}}{CaH_4(PO_4)_2} + \underset{\substack{\text{Calcium}\\ \text{chloride.}}}{2CaCl_2}$$

This acid solution is then filtered from insoluble matter, and ammonia added to precipitate the pure calcium phosphate.

$$\underset{\substack{\text{Calcium}\\ \text{acid phosphate.}}}{CaH_4(PO_4)_2} + \underset{\substack{\text{Calcium}\\ \text{chloride.}}}{2CaCl_2} + \underset{\substack{\text{Ammonium}\\ \text{hydrate.}}}{4NH_4HO} =$$

$$\underset{\substack{\text{Calcium}\\ \text{phosphate.}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Ammonium}\\ \text{chloride.}}}{4NH_4Cl} + \underset{\text{Water.}}{4H_2O}$$

Calcium hypophosphite. (*See* page 181.)

Calcium sulphide (CaS) is prepared by heating lime in a stream of sulphuretted hydrogen gas,—

$$\underset{\substack{\text{Calcium}\\\text{oxide.}}}{CaO} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{H_2S} = \underset{\substack{\text{Calcium}\\\text{sulphide.}}}{CaS} + \underset{\text{Water;}}{H_2O}$$

or by heating a mixture of calcium sulphate and charcoal, the latter reducing the sulphate to sulphide,—

$$\underset{\substack{\text{Calcium}\\\text{sulphate.}}}{CaSO_4} + \underset{\text{Carbon.}}{4C} = \underset{\substack{\text{Calcium}\\\text{sulphide.}}}{CaS} + \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{4CO}$$

If calcium sulphide be exposed to light, it is afterwards for some time phosphorescent in the dark. It is the chief constituent of *Balmain's luminous paint.* If treated with an acid, such as hydrochloric acid, sulphuretted hydrogen gas is evolved, and in this way is obtained in a very pure state, such as is required in toxicological investigations.

$$\underset{\substack{\text{Calcium}\\\text{sulphide.}}}{CaS} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Calcium}\\\text{chloride.}}}{CaCl_2} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{H_2S}$$

Chlorinated lime, or **bleaching powder** (*see* page 138).

Tests for Calcium.

(i) Ammonium oxalate or carbonate gives, with a solution of a calcium salt, a white precipitate of calcium oxalate or carbonate; the oxalate is insoluble in acetic acid, but soluble in hydrochloric acid; the carbonate dissolves in both acids.

(ii) If a calcium salt be introduced into the Bunsen flame, on a piece of platinum wire previously moistened with hydrochloric acid, an orange red colour is communicated to the flame.

BARIUM.

Symbol, Ba ; *dyad ; atomic weight,* 137·4.

The salts of barium have a high specific gravity ; hence the derivation of the name from *βαρὺς, heavy* ; they are poisonous, the antidote is sodium or magnesium sulphate.

Natural compounds of barium.—(i) *Witherite* is the native carbonate of barium. (ii) *Heavy spar* is the native sulphate of barium.

Preparation and properties of the metal barium.—Barium is said to have been prepared in a similar manner to calcium, by electrolysis of the fused chloride. It is of a pale yellow colour, and possesses very similar properties to those of calcium.

Barium oxide or **baryta** (BaO).—This oxide is most conveniently prepared by heating the nitrate,

$$\underset{\text{Barium nitrate}}{2Ba(NO_3)_2} = \underset{\text{Barium oxide.}}{2BaO} + \underset{\text{Nitrogen tetroxide}}{4NO_2} + \underset{\text{Oxygen}}{O_2}$$

When water is added to barium oxide, evolution of heat takes place, and *barium hydrate* or *slaked baryta* ($Ba(HO)_2$) is produced, the reaction being similar to that which occurs during the slaking of lime. Barium forms a crystalline hydrate ($Ba(HO)_2 + 8H_2O$) which is much more soluble in water than calcium hydrate ; its solution is known as *baryta water*, and, like lime-water, if exposed to the air it absorbs carbon dioxide, producing a white deposit of barium carbonate.

Barium dioxide, or **barium peroxide** (BaO_2).—This oxide is prepared by heating baryta to a dull red heat in a stream of air or oxygen.

$$\underset{\text{Baryta.}}{2BaO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Barium dioxide}}{2BaO_2}$$

for Co_2 than lime water.

If the higher oxide be further heated it is converted into the lower oxide, with evolution of oxygen; in this way pure oxygen may be obtained from the air (*see* page 75). Barium dioxide is also employed in the preparation of hydrogen dioxide (*see* page 92). BaO_2 + any

BARIUM SALTS.

Barium nitrate ($Ba(NO_3)_2$) is prepared either by dissolving the carbonate in nitric acid, or by reducing the sulphate to sulphide by heating with charcoal, and then dissolving the sulphide in nitric acid.

Barium chloride ($BaCl_2 + 2H_2O$) is prepared by processes similar to those used for obtaining the nitrate, with the substitution of hydrochloric for nitric acid.

Tests for Barium.

(i) Barium salts give, with calcium sulphate solution, an immediate white precipitate of barium sulphate, which is insoluble in either hydrochloric or nitric acids.

(ii) Solution of potassium chromate gives a yellow precipitate of barium chromate with barium salts; this precipitate is insoluble in acetic acid, but is soluble in either hydrochloric or nitric acids.

(iii) If a barium salt be introduced into the Bunsen flame, on a piece of platinum wire previously moistened with hydrochloric acid, a yellowish-green colour is communicated to the flame.

STRONTIUM.

Symbol, Sr; *dyad; atomic weight*, 87·6.

Strontium occurs in nature as the carbonate *strontianite*, and as the sulphate *celestine*. The salts of strontium are not of any medical importance; they are prepared by processes similar to those employed in the manufacture of the calcium and barium salts.

Strontium hydrate is used in sugar refining.

Test for Strontium.

Strontium salts when introduced into the Bunsen flame on a piece of platinum wire previously moistened with hydrochloric acid, communicate a beautiful crimson colour to the flame. The nitrate and chlorate are on this account largely employed by firework manufacturers.

CHAPTER IV.

MAGNESIUM—ZINC—CADMIUM—MERCURY.

Magnesium—Natural Compounds of Magnesium—Preparation and Properties of the Metal Magnesium—Preparation of the Magnesium Salts—Test for Magnesium—Zinc—Natural Compounds of Zinc—Preparation and Properties of the Metal Zinc—Preparation of the Zinc Salts—Tests for Zinc—Cadmium—Mercury—Occurrence in Nature—Preparation and Properties of the Metal Mercury—Action of Acids on Mercury—Preparation of the Mercurous and Mercuric Salts—Tests for Mercury—Distinguishing Tests between Mercurous and Mercuric Salts—Points of Resemblance between the Metals in this group.

MAGNESIUM.

Symbol, Mg; *dyad; atomic weight,* 24·3; *specific gravity,* 1·75.

Natural compounds of magnesium.—(i) The carbonate occurs in nature in a fairly pure form as *magnesite* ($MgCO_3$), and as a double carbonate of magnesium and calcium in *dolomite.* (ii) Magnesium sulphate is found in certain mineral spring waters; in Epsom spring waters, in England; in Friedrichshall water, in Germany; and in Hunyadi Jánós water, in Hungary. (iii) Various compounds of magnesium and silica occur in nature; *talc* is magnesium silicate; *meerschaum* is a hydrated magnesium silicate; *asbestos* is a double silicate of magnesium and calcium.

Preparation and properties of the metal magnesium.—Magnesium is prepared by heating in a crucible a mixture of magnesium chloride and the metal sodium, when the latter abstracts the chlorine, forming sodium chloride, and the metal magnesium sinks to the bottom of the crucible. Magnesium is made into ribbon or wire for burning purposes, in order to produce the powerful light known as the *magnesium light.* When burnt, it produces a white ash of magnesium oxide, or magnesia; it melts at 633°.

Magnesium oxide or magnesia (MgO).—This is obtained by heating the basic magnesium carbonate.

$$\underset{\text{Basic magnesium carbonate.}}{3MgCO_3, Mg(HO)_2} = \underset{\text{Magnesium oxide.}}{4MgO} + \underset{\text{Carbon dioxide.}}{3CO_2} + \underset{\text{Water.}}{H_2O}$$

There are two varieties of the oxide, *light magnesia* and *heavy magnesia;* they are respectively prepared by the action of heat on the light and heavy carbonates. The old name for these preparations was "calcined magnesia."

MAGNESIUM SALTS.

Magnesium sulphate ($MgSO_4 + 7H_2O$), commonly known as *Epsom salts*, on account of its natural occurrence in Epsom spring waters, is prepared by dissolving the native magnesium carbonate in diluted sulphuric acid, concentrating the liquor, and allowing the salt to crystallise out.

$$\underset{\text{Magnesium carbonate.}}{MgCO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Magnesium sulphate.}}{MgSO_4} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Epsom salts resemble remarkably in their crystalline appearance the crystals of zinc sulphate, and also to a certain extent the crystals of oxalic acid, both of which poisonous materials have been mistaken for Epsom salts. From zinc sulphate, Epsom salts may be distinguished by its solution yielding no precipitate.

either with ammonium sulphide, or with potassium ferrocyanide, whereas zinc sulphate yields a white precipitate with both reagents; from oxalic acid, Epsom salts may be distinguished by being neutral to test-paper, whereas the former is strongly acid. Oxalic acid, when heated on a knife blade or platinum foil, leaves no residue; both zinc sulphate and magnesium sulphate leave, when heated strongly, an infusible residue of their respective oxides.

Magnesium carbonate ($3MgCO_3, Mg(HO)_2$).—The normal magnesium carbonate ($MgCO_3$) occurs native in magnesite and dolomite; the carbonate that is used in medicine, and which is obtained by precipitation, is a basic carbonate, consisting of three molecules of the carbonate to one of the hydrate. It is prepared by mixing solutions of magnesium sulphate and sodium carbonate, when it is thrown down as a white precipitate.

$$\underset{\substack{\text{Magnesium}\\\text{sulphate.}}}{4MgSO_4} + \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{4Na_2CO_3} + \underset{\text{Water}}{H_2O} =$$

$$\underset{\text{Magnesium carbonate.}}{3MgCO_3, Mg(HO)_2} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{4Na_2SO_4} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2}$$

There are two forms of magnesium carbonate employed in medicine, the *light carbonate* and the *heavy carbonate.* The former, which is a very fine and light precipitate, is prepared by mixing somewhat diluted and cold solutions of magnesium sulphate and sodium carbonate; the latter, which is a dense and more compact precipitate, is prepared by mixing strong and hot solutions of the same salts.

Magnesium bicarbonate ($Mg(HCO_3)_2$).—This soluble salt is contained in fluid magnesia (*Liquor magnesii carbonatis*, B. P.); it is prepared by passing a stream of carbon dioxide gas through water in which magnesium carbonate is suspended.

$$\underset{\text{Basic magnesium carbonate.}}{3MgCO_3, Mg(HO)_2} + \underset{\text{Carbon dioxide.}}{5CO_2} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Magnesium bicarbonate.}}{4Mg(HCO_3)_2}$$

If this solution be heated, carbon dioxide is evolved, and the magnesium carbonate is deposited.

Magnesium citrate ($Mg_3(C_6H_5O_7)_2$). — This salt is contained in the *Liquor magnesii citratis*, which is prepared by dissolving the basic carbonate in solution of citric acid. "Effervescing citrate of magnesia" is a granular preparation largely used as a mild saline purgative, and effervescing when mixed with water; it consists of sodium bicarbonate, citric and tartaric acids, magnesium carbonate or sulphate, and sugar. Many specimens, however, contain no magnesium salt.

Test for Magnesium.

The presence of magnesium can only be proved after the removal of the other alkaline earth metals, viz. calcium, barium, and strontium; these metals are precipitated by ammonium carbonate in presence of ammonium chloride, whereas, under such conditions, magnesium is not precipitated, the ammonium chloride keeping the magnesium carbonate in solution. To test for magnesium, it is therefore necessary to add to the solution ammonium chloride and ammonium carbonate, and warm; if calcium, barium, or strontium are present, they will be precipitated, and on filtering from the precipitate, the presence of magnesium in the filtrate can be demonstrated by the addition of solution of ammonia and of sodium phosphate, when a white granular or crystalline precipitate (ammonio-magnesium phosphate, $MgNH_4PO_4$) will be thrown down. Since the metals calcium, barium, and strontium all yield precipitates with sodium phosphate, the necessity for removing them before testing for magnesium is obvious.

ZINC

Symbol, Zn; *molecule*, Zn; *dyad; atomic weight*, 65·4; *molecular weight*, 65·4; *specific gravity*, 7·15.

Zinc is one of the elements containing only one atom in the molecule.

Natural compounds of zinc.—(i) *Calamine*, the native carbonate of zinc ($ZnCO_3$); it is of a yellowish-white colour, from a small quantity of iron or manganese contained in it, and is used in surgery in the form of an ointment and lotion. (ii) *Blende*, the native sulphide of zinc (ZnS). (iii) The red oxide (ZnO), the red colour is due to manganese. (iv) Zinc silicate ($Zn_2SiO_4 + H_2O$).

Preparation of the metal zinc.—The zinc ore, either calamine or blende, is first heated or roasted in the air, to convert it into the zinc oxide, which is then reduced to the metal by heating with charcoal or fine coal. Since zinc is a volatile metal, it is prepared by a process of distillation. The mixture of zinc oxide and charcoal or coal is placed in tube-shaped retorts (R) of fire clay, to the open end a conical clay pipe (*a*) is fitted, and to this is fixed an iron condenser (*b*, Fig. 23).

On strongly heating, the zinc is set free by the reducing action of the carbon on the zinc oxide, and passes along the pipe in the form of vapour, which in the cooler portion of the pipe condenses to molten zinc; from time to time the iron condenser is taken away, and the melted zinc scraped out from the conical clay pipe into a ladle, until all the zinc has been distilled over. Zinc prepared in this manner is generally impure, from the presence of small quantities of arsenic, from which it can be purified by well stirring with the molten zinc some potassium nitrate, which converts the arsenic into potassium arseniate.

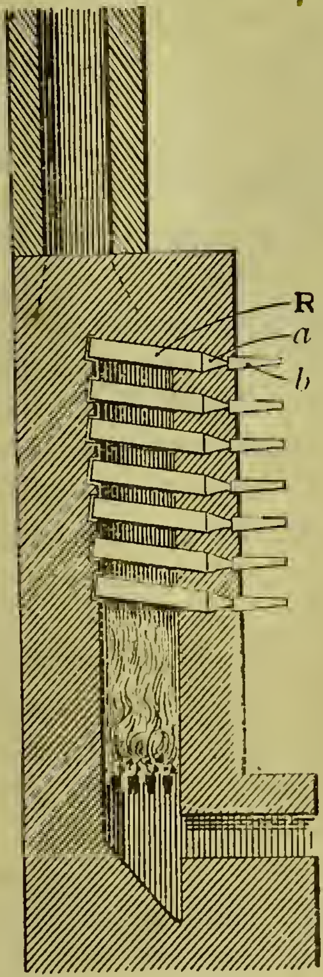


Fig. 23.—Belgian Zinc Furnace-Section.

Granulated zinc, the form in which the metal is commonly employed in the preparation of hydrogen, is obtained by pouring melted zinc from a height into water.

Properties of the metal zinc.—Zinc is a bluish-white hard metal; if heated to 100°—150° it becomes soft and malleable, so that it can be rolled into thin plates; at 200° it is quite brittle, and can then be readily reduced to powder; at 419° it melts, and boils at a bright-red heat (about 940°); when strongly heated in the air it burns with a bright bluish flame, forming light white flocks of zinc oxide. In moist air it oxidises, becoming covered with a very thin film of zinc oxide, which, however, is a very compact film, and effectually checks any further oxidation; in this respect it is very unlike the metal iron, which in moist air oxidises or rusts continuously, and so becomes in time thoroughly corroded. Zinc is employed for coating iron vessels, etc., to prevent their rusting, such coated iron being known as *galvanised iron*.

Zinc enters into the composition of some important alloys. *Brass* is an alloy of zinc and copper; *German silver* is an alloy of zinc, copper, and nickel. *Galvanised iron*, as we have seen, is prepared by dipping clean iron into molten zinc, and so coating the iron with a covering of zinc. Zinc is readily acted on by most acids; dilute sulphuric and hydrochloric acids attack it, forming respectively zinc sulphate and chloride, with evolution of hydrogen. Moderately diluted nitric acid is peculiar in its action on zinc, producing zinc nitrate and ammonia gas, the latter, however, not escaping, but being, immediately it is formed, converted by some of the nitric acid into ammonium nitrate.

$$\underset{\text{Zinc.}}{4Zn} + \underset{\text{Nitric acid.}}{9HNO_3} = \underset{\text{Zinc nitrate.}}{4Zn(NO_3)_2} + \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Water.}}{3H_2O}$$

[illegible] NH_4NO_3 heated

Zinc oxide (ZnO) is prepared either by burning the metal zinc in air, or by heating the basic zinc carbonate.

$$\underset{\text{Basic zinc carbonate.}}{ZnCO_3, 2Zn(HO)_2} = \underset{\text{Zinc oxide.}}{3ZnO} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{2H_2O}$$

Zinc oxide under the name of *zinc-white* is used as a paint; it possesses this advantage over white-lead, that it is not blackened by sulphuretted hydrogen, whereas white-lead paint slowly blackens on account of the small quantities of sulphuretted hydrogen present in the air of towns and dwelling-houses. The covering power or "body" of zinc-white is, however, not nearly so great as that of white-lead.

ZINC SALTS.

Zinc sulphate ($ZnSO_4 + 7H_2O$) is prepared by the action of dilute sulphuric acid on zinc.

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + \underset{\text{Hydrogen.}}{H_2}$$

Zinc sulphate occurs in small crystals, very much resembling magnesium sulphate, for which it is apt to be mistaken. For the methods of distinguishing the two salts, *see* page 243.

Zinc sulphate is occasionally termed *white vitriol;* it is an emetic.

Zinc chloride ($ZnCl_2$) is prepared in solution by the action of hydrochloric acid on zinc.

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Zinc chloride.}}{ZnCl_2} + \underset{\text{Hydrogen.}}{H_2}$$

It is very poisonous; it is used as a disinfectant, under the name of "Burnett's fluid;" it coagulates albumen. When melted it dissolves metallic oxides, and is largely used in soldering with tin and lead alloys. It is a white deliquescent solid.

Zinc carbonate ($ZnCO_3$, $2Zn(HO)_2$).—The normal carbonate ($ZnCO_3$) only occurs in nature as *calamine*. The precipitated carbonate is a basic carbonate, or double carbonate and hydrate, and is prepared by mixing solutions of zinc sulphate and sodium carbonate, when it is thrown down as a white precipitate.

$$\underset{\text{Zinc sulphate.}}{3ZnSO_4} + \underset{\text{Sodium carbonate.}}{3Na_2CO_3} + \underset{\text{Water.}}{2H_2O} =$$

$$\underset{\text{Basic zinc carbonate.}}{ZnCO_3,2Zn(HO)_2} + \underset{\text{Sodium sulphate.}}{3Na_2SO_4} + \underset{\text{Carbon dioxide.}}{2CO_2}$$

Zinc acetate ($Zn(C_2H_3O_2)_2$) is prepared by the action of acetic acid on the basic zinc carbonate.

Zinc valerianate ($Zn(C_5H_9O_2)_2 + 2H_2O$) is prepared by mixing strong and hot solutions of zinc sulphate and sodium valerianate; on cooling, the valerianate of zinc separates out as a crystalline white substance.

IV.

Tests for Zinc.

(i) Ammonium sulphide gives in neutral or alkaline zinc solutions a white precipitate of zinc sulphide (ZnS). This is a characteristic reaction, as zinc sulphide is the only white sulphide capable of being precipitated.

(ii) Solution of ammonia gives a white precipitate of zinc hydrate ($Zn(HO)_2$), readily soluble in excess of ammonia. From this solution in the excess of ammonia the zinc may be precipitated as the white sulphide by the addition of ammonium sulphide.

(iii) When heated with the blowpipe on charcoal, zinc salts leave a residue of zinc oxide which glows in the flame, turning yellow when hot and white on cooling. If this be moistened with cobalt nitrate and again made red hot, a bright green mass is obtained.

(iv) Potassium ferrocyanide gives a white precipitate of zinc ferrocyanide.

CADMIUM.

Symbol, Cd; *atomic weight*, 112·3; *specific gravity*, 8·6.

Cadmium is a tin-white metal; it occurs as sulphide with zinc ores, and closely resembles that metal in its properties and its compounds. It melts at 320° and boils at 760°; it burns with a bright flame, forming a brown oxide. Its sulphide is bright yellow and is used as a pigment (*cadmium yellow*).

MERCURY.

Cinnabar = HgS.

Symbol, Hg; *molecule*, Hg; *dyad*; *atomic weight*, 200; *molecular weight*, 200.

Natural compounds of mercury.—(i) The chief natural compound of mercury is *cinnabar*, a sulphide of mercury (HgS), which is found in masses of a dark red colour. (ii) Mercury is occasionally found in the free state in small quantities.

Preparation of the metal mercury.—It is obtained from cinnabar by heating it with quicklime in retorts, when double decomposition first takes place between the cinnabar and the lime, resulting in the formation of mercuric oxide and calcium sulphide.

$$\underset{\text{Cinnabar.}}{HgS} + \underset{\text{Lime.}}{CaO} = \underset{\substack{\text{Mercuric}\\\text{oxide.}}}{HgO} + \underset{\substack{\text{Calcium}\\\text{sulphide.}}}{CaS}$$

The mercuric oxide is then decomposed by the heat into mercury and oxygen, the mercury distilling over, and being condensed in a suitable receiver.

Mercury may also be obtained by roasting cinnabar in excess of air, and passing the resulting vapours of mercury and sulphur dioxide through a series of condensing chambers to condense the mercury.

Properties of the metal mercury.—At ordinary temperatures mercury is a heavy lustrous liquid; it is the only metal that is liquid at ordinary temperatures; it is commonly known as *quicksilver*, on account of its possessing a white colour like silver, and from its being liquid. Its specific gravity is 13·59; it solidifies at –38·8°, and boils at 357°; it volatilises slowly at ordinary temperatures; it remains unchanged in air at ordinary temperatures, but when heated to 300°, in contact with air, it oxidises, forming the red oxide of mercury. It is capable of a very fine state of division if well rubbed with certain substances, and in this finely-divided state it is employed in some medicinal preparations. Those containing such finely-divided mercury are blue pill (*Pilula hydrargyri*), grey powder (*Hydrargyrum cum creta*), and mercury ointment (*Unguentum hydrargyri*). Mercury unites with most of the metals, forming *amalgams*, the most useful of which is an amalgam of mercury and tin, which is used for silvering ordinary looking-glasses. Mercury does not unite or amalgamate with iron and platinum, hence it is generally stored in large iron bottles.

Action of acids on mercury.—Dilute sulphuric acid and hydrochloric acid have no action on mercury. Strong sulphuric acid with heat acts on mercury, forming mercuric sulphate, and evolving sulphur dioxide.

$$\underset{\text{Mercury.}}{Hg} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Mercuric sulphate.}}{HgSO_4} + \underset{\text{Sulphur dioxide.}}{SO_2} + \underset{\text{Water.}}{2H_2O}$$

Nitric acid acts on mercury, producing different mercury salts, accordingly as strong or dilute nitric acid is employed with heat or without. Strong nitric acid with heat forms mercuric nitrate, with evolution of nitrogen dioxide.

$$\underset{\text{Mercury.}}{3Hg} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Mercuric nitrate.}}{3Hg(NO_3)_2} + \underset{\text{Nitrogen dioxide.}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

Moderately diluted nitric acid digested with mercury in the cold forms mercurous nitrate with evolution of nitric oxide.

$$\underset{\text{Mercury.}}{6Hg} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Mercurous nitrate.}}{3Hg_2(NO_3)_2} + \underset{\text{Nitrogen dioxide.}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

Aqua regia (nitro-hydrochloric acid) dissolves mercury, forming mercuric chloride, and evolving nitric oxide.

$$\underset{\text{Mercury.}}{3Hg} + \underset{\text{Hydrochloric acid.}}{6HCl} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Mercuric chloride.}}{3HgCl_2} + \underset{\text{Nitrogen dioxide.}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

Mercuric oxide (HgO).—There are two varieties of this oxide—the *red* or crystalline variety, and the *yellow* or amorphous variety. The red mercuric oxide, commonly known as *red precipitate*, is obtained as a red crystalline powder by heating mercuric nitrate alone or mixed with metallic mercury.

$$\underset{\text{Mercuric nitrate.}}{Hg(NO_3)_2} + \underset{\text{Mercury.}}{Hg} = \underset{\text{Mercuric red oxide.}}{2HgO} + \underset{\text{Nitrogen tetroxide.}}{2NO_2}$$

It may also be obtained by heating mercury with exposure to the air for some time at a temperature of 300°.

The yellow mercuric oxide is obtained as a yellow amorphous powder by precipitating a solution of mercuric chloride with any of the fixed alkalies, potash, soda, or lime.

$$\underset{\substack{\text{Mercuric}\\ \text{chloride.}}}{HgCl_2} + \underset{\substack{\text{Sodium}\\ \text{hydrate.}}}{2NaHO} = \underset{\substack{\text{Mercuric}\\ \text{(yellow) oxide.}}}{HgO} + \underset{\substack{\text{Sodium}\\ \text{chloride.}}}{2NaCl} + \underset{\text{Water.}}{H_2O}$$

The yellow mercuric oxide is contained in *yellow lotion* or *yellow wash* (*Lotio hydrargyri flava*), in which it is made by precipitating a weak solution of mercuric chloride with lime-water.

$$\underset{\substack{\text{Mercuric}\\ \text{chloride.}}}{HgCl_2} + \underset{\substack{\text{Calcium}\\ \text{hydrate.}}}{Ca(HO)_2} = \underset{\substack{\text{Mercuric}\\ \text{(yellow) oxide.}}}{HgO} + \underset{\substack{\text{Calcium}\\ \text{chloride.}}}{CaCl_2} + \underset{\text{Water.}}{H_2O}$$

Mercurous oxide (Hg_2O) is also known as *black oxide of mercury*; it is prepared by the action of one of the fixed alkalies, potash, soda, or lime, on a mercurous salt; it is contained in *black lotion* or *black wash* (*Lotio hydrargyri nigra*), in which it is obtained as a black precipitate by shaking together calomel (mercurous chloride) and lime-water.

$$\underset{\substack{\text{Mercurous}\\ \text{chloride.}}}{Hg_2Cl_2} + \underset{\substack{\text{Calcium}\\ \text{hydrate.}}}{Ca(HO)_2} = \underset{\substack{\text{Mercurous}\\ \text{oxide.}}}{Hg_2O} + \underset{\substack{\text{Calcium}\\ \text{chloride.}}}{CaCl_2} + \underset{\text{Water.}}{H_2O}$$

MERCURY SALTS.

There are two classes of mercury salts, *mercuric* and *mercurous*, in both of which the mercury is acting as a dyad; but all mercurous compounds contain in the molecule two atoms of mercury, and as these two atoms are linked together by an atom-fixing power of each, the mercury atoms only exert towards other elements the atom-fixing power of a monad. This is rendered evident by inspection of the following graphic formulæ of mercuric chloride ($HgCl_2$) and mercurous chloride (Hg_2Cl_2).

$$\underset{\text{Mercuric chloride.}}{Cl{-}Hg{-}Cl} \qquad \underset{\text{Mercurous chloride.}}{Cl{-}Hg{-}Hg{-}Cl}$$

It will be convenient to describe the various mercuric and mercurous salts together.

Mercuric sulphate ($HgSO_4 + H_2O$) is prepared by the action of strong sulphuric acid with heat on mercury.

$$\underset{\text{Mercury.}}{Hg} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Mercuric}\\\text{sulphate.}}}{HgSO_4} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{SO_2} + \underset{\text{Water.}}{2H_2O}$$

Mercuric sulphate is largely used in the preparation of mercuric chloride (corrosive sublimate), and also for preparing mercurous sulphate, from which calomel is made. Mercuric sulphate is decomposed by water, with production of a yellow basic sulphate of mercury ($HgSO_42HgO$), formerly employed in medicine under the name of *Turpeth mineral.*

$$\underset{\substack{\text{Mercuric}\\\text{sulphate.}}}{3HgSO_4} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Turpeth}\\\text{mineral.}}}{Hg_3O_2SO_4} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4}$$

Mercurous sulphate (Hg_2SO_4).—This is prepared by well rubbing mercuric sulphate with as much mercury as it already contains.

$$\underset{\substack{\text{Mercuric}\\\text{sulphate.}}}{HgSO_4} + \underset{\text{Mercury.}}{Hg} = \underset{\substack{\text{Mercurous}\\\text{sulphate.}}}{Hg_2SO_4}$$

This salt is used for the preparation of calomel; it is very apt to be contaminated with some unchanged mercuric sulphate.

Mercuric chloride ($HgCl_2$).—This important salt is also known as *perchloride of mercury*, *bichloride of mercury*, and *corrosive sublimate*. It is prepared by heating a mixture of mercuric sulphate and sodium chloride (common salt), a little black oxide of manganese being added to prevent the formation of mercurous chloride, and conveying the vapour of the mercuric chloride into a cool chamber, where it condenses to a white crystalline solid.

$$\underset{\text{Mercuric sulphate.}}{HgSO_4} + \underset{\text{Sodium chloride.}}{2NaCl} = \underset{\text{Mercuric chloride.}}{HgCl_2} + \underset{\text{Sodium sulphate.}}{Na_2SO_4}$$

Mercuric chloride is a very poisonous substance; it is soluble in water, but if the solution is kept exposed to light it slowly decomposes, depositing mercurous chloride (calomel). A weak aqueous solution of mercuric chloride (1 part in 1,000 of water) is a powerful germicide, and is largely used in surgery as an antiseptic lotion; in using it, care should be taken not to dip articles of gold, such as rings, into it, as they would quickly become coated with metallic mercury. It coagulates albumen, forming an insoluble compound; white of egg is therefore used as an antidote in cases of poisoning by corrosive sublimate.

Mercurous chloride (Hg_2Cl_2).—This largely-employed mercurial preparation is also known as *calomel* and *subchloride of mercury*. It is prepared by heating a mixture of mercurous sulphate and sodium chloride (common salt), when the calomel that is formed volatilises, and the vapour is conveyed into a cool chamber, within which it condenses to a white powder.

$$\underset{\substack{\text{Mercurous}\\\text{sulphate.}}}{Hg_2SO_4} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl} = \underset{\substack{\text{Mercurous}\\\text{chloride.}}}{Hg_2Cl_2} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4}$$

As the mercurous sulphate is apt to be contaminated with mercuric sulphate, so calomel is apt to be contaminated with corrosive sublimate formed from the mercuric sulphate; the calomel must be freed from this impurity by thoroughly washing it with hot water, until the washings cease to show the presence of corrosive sublimate, as indicated by their ceasing to give a black precipitate with ammonium sulphide. As calomel is given in fairly large doses (5 to 10 grains), it is most important that it should be thoroughly freed from the poisonous corrosive sublimate. A simple test for the detection of the latter impurity in calomel is to place some of the calomel on a clean knife-blade, moisten it with a few drops of alcohol, and allow it to remain for a few minutes, when a black spot will be produced on the blade if corrosive sublimate is present.

Another method of preparing calomel is to precipitate it from a solution of mercurous nitrate by means of hydrochloric acid.

$$\underset{\substack{\text{Mercurous}\\\text{nitrate.}}}{Hg_2(NO_3)_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Mercurous}\\\text{chloride.}}}{Hg_2Cl_2} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3}$$

This process is not employed for the preparation of the calomel used in medicine, the sublimation process always being used for the commercial production of calomel.

Mercuric iodide (HgI_2), also known as the *biniodide of mercury* and the *red iodide of mercury*, is prepared by precipitating a solution of mercuric chloride with potassium iodide. It is thrown down at first as a yellow precipitate, rapidly changing to red.

$$\underset{\text{Mercuric chloride.}}{HgCl_2} + \underset{\text{Potassium iodide.}}{2KI} = \underset{\text{Mercuric iodide.}}{HgI_2} + \underset{\text{Potassium chloride.}}{2KCl}$$

The precipitated mercuric iodide is soluble in excess of either mercuric chloride or of iodide of potassium, but especially in the latter; with excess of potassium iodide it forms a soluble double iodide ($HgI_2,2KI$), which is a very convenient and frequently employed form of administering mercury internally. This is generally done by prescribing together a suitable dose of perchloride of mercury (*Liquor hydrargyri perchloride*) with excess of potassium iodide. A weak solution of this double iodide (1 part in 2,000 or 3,000 of water) is also a powerful germicide and disinfectant, and is employed as an antiseptic lotion. *Nessler's solution* is a solution of this double iodide of mercury and potassium mixed with caustic potash. It constitutes an extremely delicate test for ammonia, and can be used for the detection of most minute quantities of ammonia in drinking waters, imparting a yellow or brownish tint to the water, according to the amount of ammonia present. This test is known as *Nessler's test.*

Mercurous iodide (Hg_2I_2), also known as the *green iodide of mercury*, is prepared by direct combination of its elements in suitable proportions—*i.e.* by rubbing 200 parts of mercury with 127 parts of iodine and a little alcohol, the latter being used to prevent elevation of temperature, due to the chemical action taking place.

Mercuric nitrate ($Hg(NO_3)_2+8H_2O$) is prepared by the action of strong nitric acid with heat on the metal mercury.

$$\underset{\text{Mercury.}}{3Hg} + \underset{\text{Nitri acid.}}{8HNO_3} = \underset{\text{Mercuric nitrate.}}{3Hg(NO_3)_2} + \underset{\text{Nitrogen dioxide.}}{2NO} + \underset{\text{Water}}{4H_2O}$$

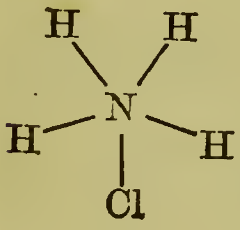
Mercurous nitrate ($Hg_2(NO_3)_2 + 2H_2O$) is prepared by the action of moderately diluted nitric acid in the cold on the metal mercury.

$$\underset{\text{Mercury.}}{6Hg} + \underset{\substack{\text{Nitric}\\ \text{acid.}}}{8HNO_3} = \underset{\substack{\text{Mercurous}\\ \text{nitrate.}}}{3Hg_2(NO_3)_2} + \underset{\substack{\text{Nitrogen}\\ \text{dioxide.}}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

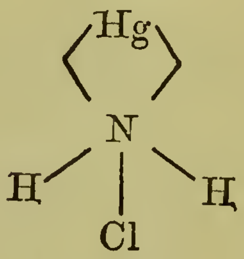
Mercuric cyanide ($Hg(CN)_2$).—If red mercuric oxide is digested in dilute hydrocyanic acid, it dissolves, and mercuric cyanide is afterwards deposited in crystals.

$$\underset{\substack{\text{Mercuric}\\ \text{oxide.}}}{HgO} + \underset{\substack{\text{Hydrocyanic}\\ \text{acid.}}}{2HCN} = \underset{\substack{\text{Mercuric}\\ \text{cyanide.}}}{Hg(CN)_2} + \underset{\text{Water.}}{H_2O}$$

Ammoniated mercury (NH_2HgCl). — This compound, commonly known as *infusible white precipitate*, is mercuric ammonium chloride; that is, it consists of ammonium chloride (NH_4Cl) from which two atoms of the monad hydrogen have been displaced by one atom of the dyad mercury, as is rendered evident by inspection of their graphic formulæ.



Ammonium chloride.



Ammoniated mercury

It is obtained as a white precipitate by pouring an excess of ammonia into a solution of mercuric chloride.

$$\underset{\text{Mercuric chloride.}}{HgCl_2} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Ammoniated mercury.}}{NH_2HgCl} + \underset{\text{Ammonium chloride}}{NH_4Cl}$$

Fusible white precipitate ($HgCl_2(NH_3)_2$) is prepared by adding a solution of mercuric chloride to a boiling solution of ammonium chloride and ammonia.

Mercuric sulphide (HgS).—This exists in nature as cinnabar; it constitutes the pigment *vermilion*, which is prepared by rubbing together mercury and sulphur, when the black amorphous mercuric sulphide is obtained, which on heating sublimes as vermilion; the composition of the sulphide is not changed by the heat, but the black amorphous sulphide becomes converted into the red crystalline variety. *Ethiop's mineral*, formerly employed in medicine, is a mixture of the black mercuric sulphide and free sulphur; it is obtained by rubbing mercury with excess of sulphur.

Mercuric oleate.—This substance, which is now frequently used as an external application in certain skin diseases, is prepared by dissolving yellow mercuric oxide in oleic acid.

Test for Mercury.

All solid mercury compounds if mixed with lime or sodium carbonate, and then heated in a dry test-tube, yield a sublimate of metallic mercury on the cool sides of the tube; this sublimate, when rubbed with a glass rod, produces the characteristic globules of mercury.

Tests for Mercuric Salts.

(i) Sulphuretted hydrogen gives a black precipitate of mercuric sulphide; if the solution of the mercuric salts is strong, the precipitate may at first come down of a yellowish-white colour; afterwards, as more sulphuretted hydrogen passes in, the light-coloured precipitate passes through successive stages of dark yellow, orange, and brown, to a black colour; these colour stages are due to the gradual displacement of the acid radicle of the mercury salt by the sulphur.

(ii) Ammonium sulphide also precipitates the black mercuric sulphide.

(iii) Potassium iodide gives with a solution of a mercuric salt a precipitate of red mercuric iodide, the precipitate being thrown down at first of a yellowish colour, rapidly changing to red; it is soluble in excess of either the mercuric salt or of potassium iodide, but especially in the latter. — Strip of Cu fo

(iv) If a solution of a mercuric salt is acidified with a few drops of hydrochloric acid, and then boiled for a few minutes with a strip of bright copper foil, the metal mercury is deposited on the surface of the strip of copper, giving to it a characteristic lustre resembling polished silver; if the strip of copper is washed with water, carefully dried, and then heated in a dry test-tube, a sublimate of metallic mercury will be obtained on the sides of the tube; this sublimate, when rubbed with a glass rod, produces the characteristic globules of mercury; or a scale of iodine may be introduced to the bottom of the tube, which is then gently warmed so as to slightly volatilise the iodine; the vapour of the iodine unites with the mercury, and converts it into the yellow iodide, which in its turn changes to the scarlet mercuric iodide.

(v) Caustic potash and caustic soda both give with solutions of mercuric salts a yellow precipitate of mercuric oxide.

Sb As S | HNO_3 [illegible] | [illegible]
KHS [illegible]
[illegible] yellow [illegible]

HCl gives white ppt.
Blackens with NH_3OH.

Tests for Mercurous Salts.

Group. I

(i) Hydrochloric acid gives, with a solution of a mercurous salt, a white precipitate of mercurous chloride (calomel); this is blackened by the addition of ammonia, owing to the formation of the black mercurous ammonium chloride (NH_2Hg_2Cl), the mercurous analogue of ammoniated mercury (NH_2HgCl). Hg_2Cl_2

(ii) Potassium iodide gives a dirty-green precipitate of mercurous iodide. "Green iodide of Hg Hg_2I_2

(iii) Caustic potash and caustic soda both give a black precipitate of mercurous oxide." Black oxide of Hg_2 = Hg_2O

6 0.5.

It will be noticed that the metals treated in this chapter form the right-hand half of the second column in the classification given on page 208. It will be convenient to note here some of their points of resemblance. They are all ductile metals and are divalent, their volatility increases as their atomic weight rises; thus, zinc boils at 940°, cadmium at 760°, mercury at 357°. Magnesium, zinc, and cadmium all burn with a flame when heated in air forming the oxides MgO, ZnO, CdO; they all form sulphates which are isomorphous and have the formula $MgSO_4 + 7H_2O$, etc.; these sulphates are soluble in water. The spectra of these three elements present many points of similarity. Mercury differs in several respects from the other members of the group, thus it forms two oxides, its sulphate is anhydrous, and it does not burn with flame when heated in the air.

IV. $SnCl_2$. gives grey ppt. of metallic Hg

AmOH | KI Green Hg_2I_2
NaOH black Hg_2O
$SnCl_2$ grey ppt of Hg.

CHAPTER V.

ALUMINIUM—TIN AND LEAD.

Aluminium—Natural Compounds of Aluminium—Preparation and Properties of the Metal Aluminium—Alums—Preparation of the Aluminium Salts—Tests for Aluminium—Tin—Preparation and Properties of the Metal Tin—Tin Salts—Tests for Tin—Lead—Occurrence in Nature—Preparation and Properties of the Metal Lead—Action of Acids on Lead—Oxides of Lead—Preparation of the Lead Salts—Tests for Lead.

ALUMINIUM.

prep'n & the Chloride

Symbol, Al; *triad; atomic weight*, 27; *specific gravity*, 2·57; *melts at* 654°.

Natural compounds of aluminium. — (i) Aluminium occurs largely in nature combined with silica; the different forms of *clay* consist of aluminium silicate; *felspar, granite, mica, alum-shale* or *schist*, all contain aluminium silicate. (ii) *Cryolite* is a double fluoride of aluminium and sodium. (iii) *Bauxite* is an impure form of aluminium hydrate. (iv) The precious stones, the *ruby* and the *sapphire*, and the polishing powder known as *emery powder*, consist mainly of aluminium oxide or alumina (Al_2O_3).

Preparation and properties of the metal aluminium.—The oxide of aluminium cannot be deprived of its oxygen by means of charcoal at any temperature, since the reaction $Al_2O_3 + 3C$ is endothermic and is attended with the *absorption* of a large amount of heat; the metal can be obtained by reducing aluminium chloride by means of the metal sodium, the sodium uniting with the chlorine, and the metal aluminium being set free. All the aluminium at the present time is obtained by the aid of electricity; pure alumina (Al_2O_3) is dissolved in fused cryolite ($3NaF, AlF_3$), and the melted liquid decomposed by a powerful current of electricity. Aluminium is a light, white metal, remaining unchanged in both dry and moist air. Dilute sulphuric and hydrochloric acids both act on the metal aluminium, forming respectively the sulphate and chloride, with evolution of hydrogen. It is practically unaffected by nitric acid; it is dissolved by alkalies and by organic acids in the presence of sodium chloride. It is much used for telescopes, opera-glasses, cooking vessels, etc., on account of its lightness. It forms a valuable alloy with copper, Cu_9Al, aluminium bronze, which is as strong as steel and has the advantage of not rusting. Aluminium is a good conductor of electricity and a very powerful reducing agent.

Aluminium oxide or **alumina** (Al_2O_3).—This oxide may be prepared either by heating the precipitated aluminium hydrate,—

$$\underset{\text{Aluminium hydrate.}}{2Al(HO)_3} = \underset{\text{Aluminium oxide.}}{Al_2O_3} + \underset{\text{Water;}}{3H_2O.}$$

or by heating ammonia alum, when ammonium sulphate and sulphur trioxide will be volatilised by the heat, the aluminium oxide being left,—

$$\underset{\text{Ammonia alum.}}{Al_2(SO_4)_3,(NH_4)_2SO_4} = \underset{\text{Aluminium oxide.}}{Al_2O_3} + \underset{\text{Ammonium sulphate.}}{(NH_4)_2SO_4} + \underset{\text{Sulphur trioxide}}{3SO_3}$$

Aluminium hydrate ($Al(HO)_3$) is prepared by the addition of an alkali to solution of ammonia alum or potash alum; it is a gelatinous precipitate, which possesses the power of fixing or combining with vegetable dyes, and hence is used as a mordant; it is also employed in the chemical treatment of sewage,

$M_2(SO_4)_3$ } 24 H_2O. = an alu
$M^I_2 SO_4$

on account of its property of entangling and carrying down suspended matters.

ALUMINIUM SALTS.

Ammonia alum ($Al_2(SO_4)_3$, $(NH_4)_2SO_4$ + $24H_2O$).—This is prepared by mixing solutions of aluminium sulphate and ammonium sulphate, evaporating the mixed solution and setting it aside, when the alum crystallises out. The aluminium sulphate is obtained either by the action of strong sulphuric acid with heat on clay, or by roasting alum-shale in the air. Alum-shale is a hardened clay containing iron pyrites (FeS_2); when roasted the sulphur becomes oxidised to sulphuric acid, which forms aluminium sulphate by its action on the silicate, ferric oxide being also produced; on boiling the roasted shale with water, the aluminium sulphate is dissolved out, ferric oxide being left insoluble.

Potash alum ($Al_2(SO_4)_3$, K_2SO_4 + $24H_2O$).—This is prepared by a process similar to that used for making ammonia alum, with the substitution of potassium sulphate for ammonium sulphate

If potash alum be deprived of its water of crystallisation by heating, the anhydrous alum is known as *burnt alum.*

There are *alums* which contain no aluminium, such as *iron alum* ($Fe_2(SO_4)_3$, K_2SO_4 + $24H_2O$), and *chrome alum* ($Cr_2(SO_4)_3$, K_2SO_4 + $24H_2O$); so that the term "alum" is used for bodies which may or may not contain aluminium. The term alum when used in this extended sense simply means a double sulphate, having the formula $M_2(SO_4)_3 + N_2SO_4 + 24H_2O$ (where M may be aluminium, ferric iron, chromium or manganese, and N potassium, sodium, ammonium, rubidium, silver, etc.), and crystallising in octahedra.

Aluminium chloride ($AlCl_3$) is prepared by passing a stream of chlorine over a mixture of alumina and charcoal raised to a red heat, when the aluminium chloride volatilises and condenses on cooling to a white solid.

$$\underset{\text{Aluminium oxide.}}{Al_2O_3} + \underset{\text{Carbon.}}{3C} + \underset{\text{Chlorine.}}{6Cl} = \underset{\text{Aluminium chloride.}}{2AlCl_3} + \underset{\text{Carbon monoxide.}}{3CO}$$

roup III

Tests for Aluminium.

(i) Aluminium salts give with solution of ammonia a white gelatinous precipitate of aluminium hydrate $Al(HO)_3$, insoluble in excess of ammonia.

(ii) With ammonium sulphide aluminium salts also give a precipitate of aluminium hydrate, sulphuretted hydrogen being evolved. Ammonium sulphide does not precipitate the sulphide, because aluminium sulphide is decomposed by water into the hydrate and sulphuretted hydrogen.

$$\underset{\text{Aluminium sulphide.}}{Al_2S_3} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Aluminium hydrate.}}{2Al(HO)_3} + \underset{\text{Sulphuretted hydrogen.}}{3H_2S}$$

(iii) With the fixed alkalies, caustic potash and caustic soda, aluminium salts yield a precipitate of aluminium hydrate, soluble in excess of either fixed alkali.

(iv) If a solid aluminium compound be heated on charcoal before the blowpipe, it leaves an infusible mass of Al_2O_3 which glows in the flame; if this be moistened with $Co(NO_3)_2$ and again made red hot, a fine blue mass is obtained.

Aluminium is the only commonly occurring metal in the third column of the classification (p. 208). The other metals in this group are rare. The oxide of thorium is the chief constituent of the Welsbach incandescent mantle (95—99 per cent.), the other constituent being oxide of cerium.

TIN.

Symbol, Sn ; *dyad and tetrad ; atomic weight*, 119 ; *specific gravity*, 7·3 ; *melts at* 232°.

Natural compounds of tin.—The principal tin ore is *tinstone* or stannic oxide (SnO_2), which is found in Cornwall, Saxony, Bohemia, Peru, Mexico, Banca, and Australia.

Preparation and properties of the metal tin.—The tin ore is first roasted to expel arsenic and sulphur, and the stannic oxide is then reduced to the metallic state by heating it with anthracite coal or powdered charcoal. Tin is a soft and very malleable metal ; it can therefore be rolled out into thin foil (tin-foil). It does not lose its lustre on exposure to the air at ordinary temperatures, and is used to coat iron to prevent the latter from rusting, *tin-plate* consisting of thin sheets of iron coated with tin. A bar of tin when bent emits a peculiar noise, the so-called *cry of tin*, produced by the friction of the crystals of the metal against one another. Tin enters into the composition of several very useful alloys ; *bronze* or *gun metal* is an alloy of copper and tin ; *britannia metal* is composed of tin and antimony ; *solder* consists of tin and lead ; *pewter* is also an alloy of tin and lead. With mercury it forms an amalgam used to coat the backs of looking-glasses.

Action of acids on the metal tin.—Hot concentrated hydrochloric acid forms stannous chloride ($SnCl_2$) with evolution of hydrogen.

$$\underset{\text{Tin.}}{Sn} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Stannous chloride.}}{SnCl_2} + \underset{\text{Hydrogen.}}{H_2}$$

Hot strong sulphuric acid forms stannous sulphate ($SnSO_4$), and liberates sulphur dioxide.

$$\underset{\text{Tin.}}{Sn} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Stannous}\\ \text{sulphate.}}}{SnSO_4} + \underset{\substack{\text{Sulphur}\\ \text{dioxide.}}}{SO_2} + \underset{\text{Water.}}{2H_2O}$$

Strong nitric acid acts energetically on tin with the production of a white powder, metastannic acid, and the evolution of nitrogen tetroxide.

$$\underset{\text{Tin}}{5Sn} + \underset{\substack{\text{Nitric}\\ \text{acid.}}}{20HNO_3} = \underset{\substack{\text{Metastannic}\\ \text{acid.}}}{H_{10}Sn_5O_{15}} + \underset{\substack{\text{Nitrogen}\\ \text{tetroxide.}}}{20NO_2} + \underset{\text{Water.}}{5H_2O}$$

Stannic oxide (SnO_2) is prepared by heating metastannic acid, the product of the action of nitric acid on tin.

$$\underset{\substack{\text{Metastannic}\\ \text{acid.}}}{H_{10}Sn_5O_{15}} = \underset{\substack{\text{Stannic}\\ \text{oxide.}}}{5SnO_2} + \underset{\text{Water.}}{5H_2O}$$

Stannic oxide is used, under the name of *putty-powder*, as a polishing powder for plate, lenses, etc.

TIN SALTS.

There are two classes of tin salts, *stannous* and *stannic;* in the former the tin is only exerting one half of its atomicity, viz. as a dyad; in the latter it is exerting its full atomicity as a tetrad.

Stannous chloride ($SnCl_2 + 2H_2O$) is prepared by the action of hot concentrated hydrochloric acid on tin. This salt is used commercially, under the name of *tin-salt*, in dyeing and for purposes of reduction.

Stannic chloride ($SnCl_4$) is prepared by passing chlorine into a solution of stannous chloride, or by c H_2S | AmS | Am CO_3 | $HgCl_2$ = no ppt.

passing dry chlorine over melted tin; it is a fuming liquid.

Tests for Tin.

(i) Sulphuretted hydrogen gives with an acidified solution of a stannous salt a brownish-black precipitate of stannous sulphide, and with an acidified solution of a stannic salt a yellow precipitate of stannic sulphide; both sulphides are soluble in ammonium sulphide.

(ii) Soluble stannous salts act as reducing agents, whereas stannic salts have no reducing action. For instance, if a solution of stannous chloride be added to a solution of mercuric chloride, calomel (mercurous chloride) will be thrown down, owing to the stannous chloride abstracting one-half of the chlorine from the mercuric chloride to form stannic chloride.

$$\underset{\text{Mercuric chloride.}}{2HgCl_2} + \underset{\text{Stannous chloride.}}{SnCl_2} = \underset{\text{Mercurous chloride.}}{Hg_2Cl_2} + \underset{\text{Stannic chloride.}}{SnCl_4}$$

If more stannous chloride be now added, it will abstract all the chlorine from the precipitated calomel, forming the metal mercury in a fine state of division, and more stannic chloride.

$$\underset{\text{Mercurous chloride.}}{Hg_2Cl_2} + \underset{\text{Stannous chloride.}}{SnCl_2} = \underset{\text{Mercury.}}{2Hg} + \underset{\text{Stannic chloride}}{SnCl_4}$$

On account of the white and subsequently grey appearances of the precipitate this test was formerly known as the *magpie test for mercury.*

(iii) If a solid tin compound be heated on charcoal with potassium cyanide and sodium carbonate, a white malleable globule of tin is obtained.

-ous H_2S | AmS | [illegible] Sn
$HgCl_2$ = white

LEAD.

Symbol, Pb; *dyad; atomic weight*, 207; *specific gravity*, 11·2; *melts at* 326°.

Natural compounds of lead.—The principal lead compound occurring in nature is *galena*, sulphide of lead (PbS), which always contains small quantities of sulphide of silver; lead is also naturally found in small quantities as the sulphate and carbonate.

Preparation of the metal lead.—The principal process for the extraction of lead from galena is known as the *air reduction process.* It consists in roasting the galena in a furnace in a current of air, so as to convert it, in part, into the sulphate and oxide.

$$\underset{\text{Galena.}}{PbS} + \underset{\text{Oxygen.}}{2O_2} = \underset{\text{Lead sulphate.}}{PbSO_4}$$

$$\underset{\text{Galena.}}{2PbS} + \underset{\text{Oxygen.}}{3O_2} = \underset{\substack{\text{Lead}\\\text{oxide.}}}{2PbO} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{2SO_2}$$

The current of air is then shut off, and the temperature of the furnace is raised, when the undecomposed galena reduces both the sulphate and oxide to the metallic state, with evolution of sulphur dioxide.

$$\underset{\substack{\text{Lead}\\\text{sulphate.}}}{PbSO_4} + \underset{\text{Galena.}}{PbS} = \underset{\text{Lead}}{2Pb} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{2SO_2}$$

$$\underset{\substack{\text{Lead}\\\text{oxide.}}}{2PbO} + \underset{\text{Galena.}}{PbS} = \underset{\text{Lead.}}{3Pb} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{SO_2}$$

Lead thus prepared contains silver, which, if present in sufficient quantity to pay for its extraction, is obtained by converting the lead into lead oxide, which is removed, the silver remaining unchanged. The process by which this is effected is called the *cupellation process;* it consists in roasting the lead in a reverberatory furnace (Fig. 24), the floor or hearth of which is lined with porous clay or bone ash; the lead (A) melts and oxidises to lead oxide under the influence of blasts of air admitted through openings (*a a*); most of this lead oxide in a molten condition flows away by side openings, whilst the remainder is absorbed by the porous clay or bone-ash, pure silver being finally left on the hearth of the furnace in a molten state. From the lead oxide produced in this process, metallic lead may be obtained by reduction with charcoal or coal. The removal of silver from a quantity of lead, in the metallic state, may be effected by means of *Pattinson's process,* which depends upon the fact that the metal lead is less easily fusible than an alloy of silver and lead. The lead containing the silver is melted and then allowed to cool gradually; the part solidifying out first consists of crystals of pure lead, which can be raked out by means of a perforated iron ladle; by a systematic repetition of this process, lead containing 3 to 4 oz. of silver per ton can be separated into a portion containing less than 1 oz. per ton and

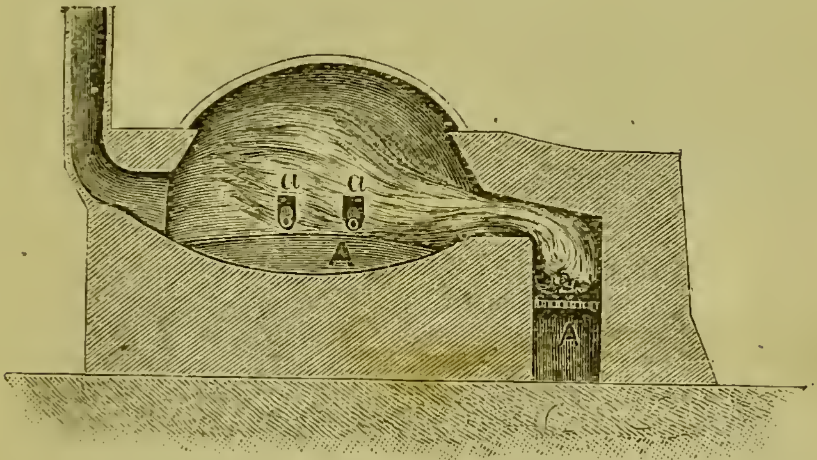


Fig. 24.—Section of the Furnace Employed in the Cupellation Process.

a rich alloy containing 75—80 oz., which is submitted to the cupellation process. Small quantities of silver can also be separated from lead by agitating it with 5 per cent. of zinc, the zinc dissolves out the silver from the melted lead and rises to the top. The zinc is then distilled off from the silver. (*Parkes' process.*)

Properties of the metal lead.—Lead is a lustrous, bluish-grey metal, soft enough to be cut with a knife, and to leave a mark on paper when drawn across it; it is malleable and ductile, but is not a good conductor of heat and electricity as compared with many other metals. If lead is exposed to perfectly dry air, it does not oxidise or tarnish, but if exposed to moist air, it soon becomes covered with a film of the double carbonate and hydrate of lead; similarly, if lead is immersed in distilled water *which has been boiled* to deprive it of all dissolved air, it remains unaffected by the water, but soft water containing air in solution attacks lead, the oxygen of the air forming lead oxide, which is then dissolved by the water as lead hydrate in small but appreciable quantities. This is one way in which a drinking water, passing through leaden pipes, may become contaminated with lead. The corrosive action of a water on lead is much increased by the presence in it of chlorides, nitrates, nitrites, and of ammonia, whereas the presence of sulphates, of calcium carbonate (held in solution as bicarbonate by a moderate excess of carbon dioxide), and of phosphates, hinders corrosion. Some soft waters, notably some moorland waters, have a powerfully solvent action upon lead, due in some cases, perhaps, to the presence of acids in the water, either humic or ulmic acid derived from the soil, and whole villages have thus been poisoned; hard water, such as that from the Thames, the Trent, etc., does not act upon lead.

Metallic lead is largely used in the manufacture of pipes, as a covering for roofs, etc. Lead is contained in several alloys, the most important of which are, *type-metal*, an alloy of lead, antimony, and tin; *pewter* and *soft solder*, alloys of lead and tin; *shot*, an alloy of lead with a small quantity of arsenic (not more than 0·8 part in 100), which possesses the property of hardening the lead.

Action of acids on the metal lead.—Hydrochloric and sulphuric acids have no action on lead in the cold, but both acids attack this metal when boiling and concentrated. Nitric acid readily acts on lead, forming lead nitrate, and evolving nitrogen dioxide.

$$\underset{\text{Lead.}}{3Pb} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{8HNO_3} = \underset{\substack{\text{Lead}\\\text{nitrate.}}}{3Pb(NO_3)_2} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

Lead oxides.—There are three important oxides of lead, the *oxide*, *dioxide*, and *red lead*.

PbO	Lead oxide.
Pb_3O_4	Red lead.
PbO_2	Lead dioxide or peroxide.

yellow

Lead oxide (PbO) is prepared by the oxidation of the metal lead, by roasting it in air. In the amorphous state it forms a dirty yellow powder (*massicot*); if fused and solidified, it forms brighter, reddish-yellow scales (*litharge*).

This oxide is largely used in the manufacture of flint glass, and as a cheap glaze for earthenware. Nitric acid dissolves litharge, forming lead nitrate and water.

$$\underset{\substack{\text{Lead}\\\text{oxide.}}}{PbO} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3} = \underset{\substack{\text{Lead}\\\text{nitrate.}}}{Pb(NO_3)_2} + \underset{\text{Water.}}{H_2O}$$

Hydrochloric acid and litharge form lead chloride and water.

$$\underset{\text{Lead oxide.}}{PbO} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Lead chloride.}}{PbCl_2} + \underset{\text{Water.}}{H_2O}$$

Red lead (Pb_3O_4), also known as *minium*, is prepared by heating lead oxide (PbO) in air to 400° for some time, when it absorbs oxygen and, becoming of a bright red colour, produces red lead. If red lead be strongly heated, it liberates the oxygen absorbed from the air, and returns to the condition of litharge; nitric acid decomposes it, dissolving two-thirds of the lead, and leaving unattacked the other third as lead dioxide (PbO_2); hydrochloric acid warmed with red lead forms lead chloride with evolution of chlorine, the latter being produced by the action of the hydrochloric acid on the lead dioxide (*see* below).

Lead dioxide (PbO_2) is also known as *lead peroxide*, and, on account of its brown colour with a purple tinge, is sometimes called the *puce-coloured oxide of lead*. It is obtained, as previously stated, by the action of nitric acid on red lead. On account of this action of nitric acid, it has been suggested that red lead is a compound of two molecules of litharge combined with one molecule of the peroxide ($2PbO,PbO_2$).

$$\underset{\text{Red lead.}}{Pb_3O_4} + \underset{\text{Nitric acid.}}{4HNO_3} = \underset{\text{Lead nitrate.}}{2Pb(NO_3)_2} + \underset{\text{Lead dioxide.}}{PbO_2} + \underset{\text{Water.}}{2H_2O}$$

Lead dioxide if heated loses one-half of its oxygen, and is converted into the monoxide; hydrochloric acid acts on it forming lead chloride, with evolution of chlorine.

$$\underset{\text{Lead dioxide.}}{PbO_2} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Lead chloride.}}{PbCl_2} + \underset{\text{Chlorine.}}{Cl_2} + \underset{\text{Water.}}{2H_2O}$$

SALTS OF LEAD.

tharge PbO

Lead acetate ($Pb(C_2H_3O_2)_2 + 3H_2O$).—This salt, on account of its sweet taste, is commonly known as *sugar of lead*; it is prepared by dissolving litharge in acetic acid with heat.

$$\underset{\text{Lead oxide.}}{PbO} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2} = \underset{\text{Lead acetate.}}{Pb(C_2H_3O_2)_2} + \underset{\text{Water.}}{H_2O}$$

Lead oxyacetate ($Pb_2O(C_2H_3O_2)_2$).—This basic lead acetate is prepared by boiling a solution of lead acetate with lead oxide.

$$\underset{\text{Lead acetate.}}{Pb(C_2H_3O_2)_2} + \underset{\text{Lead oxide.}}{PbO} = \underset{\text{Lead oxyacetate.}}{Pb_2O(C_2H_3O_2)_2}$$

Liquor plumbi subacetatis fortis is a strong solution of this oxyacetate, and is frequently termed *Goulard's extract*; a weaker solution of it is the *Liquor plumbi subacetatis dilutus*, which is frequently used as a lotion, and is commonly known as *Goulard water*.

Lead nitrate ($Pb(NO_3)_2$) is prepared by the action of nitric acid on litharge, or on the metal lead.

harge PbO metal [illegible]

$$\underset{\text{Litharge.}}{PbO} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Lead nitrate.}}{Pb(NO_3)_2} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\text{Lead.}}{3Pb} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Lead nitrate.}}{3Pb(NO_3)_2} + \underset{\text{Nitrogen dioxide.}}{2NO} + \underset{\text{Water}}{4H_2O}$$

White lead or basic lead carbonate ($2PbCO_3, Pb(HO)_2$).—This substance, which is so largely used as a white paint, is not the normal lead carbonate ($PbCO_3$), but a compound containing carbonate and hydrate of lead. There are two methods of preparing it.

(i) *The English* or *French process* consists in passing carbon dioxide gas through a solution of lead oxyacetate, when that portion of the lead not in union with the acetic radicle is precipitated as *white lead.*

$$\underset{\text{Lead oxyacetate.}}{3Pb_2O(C_2H_3O_2)_2} + \underset{\text{Carbon dioxide.}}{2CO_2} + \underset{\text{Water.}}{H_2O} =$$

$$\underset{\text{White lead.}}{2PbCO_3, Pb(HO)_2} + \underset{\text{Lead acetate.}}{3Pb(C_2H_3O_2)_2}$$

The lead acetate remaining in solution can then be boiled with litharge, and so a fresh batch of the oxyacetate will be obtained for further treatment with carbon dioxide.

(ii) *The Dutch process* also consists in decomposing lead oxyacetate with carbon dioxide in presence of moisture, but an entirely different arrangement is adopted.

Metallic lead is cast into gratings, so as to expose as large a surface of the metal as possible, and these are suspended in earthenware pots containing a layer of vinegar at the bottom; the pots are embedded in spent tan spread on the floor of a shed. The acetic acid of the vinegar and the oxygen of the air attack the lead, forming an oxyacetate, which is immediately decomposed, by the carbon dioxide and moisture evolved from the fermenting spent tan, into white lead; the action is allowed to go on until the conversion is complete, when the "stack" is taken down, and the white lead ground and washed. White lead prepared by this process is more compact, or has more *body*, than that made by the English or French process, and is therefore preferred for painting purposes; when used as a paint white lead slowly darkens, from traces of sulphuretted hydrogen in the air forming the black sulphide of lead.

Lead iodide (PbI_2) is prepared by precipitating a solution of lead acetate or lead nitrate with potassium iodide.

$Pb(C_2H_3O_2)_2$	+	$2KI$	=	PbI_2	+	$2KC_2H_3O_2$
Lead acetate.		Potassium iodide.		Lead iodide.		Potassium acetate.

Iodide of lead is a bright yellow-coloured precipitate, insoluble in cold water, but soluble in hot water.

Lead chromate ($PbCrO_4$) is prepared by precipitating a solution of lead acetate or lead nitrate with potassium chromate.

$Pb(NO_3)_2$	+	K_2CrO_4	=	$PbCrO_4$	+	$2KNO_3$
Lead nitrate.		Potassium chromate.		Lead chromate.		Potassium nitrate.

Lead chromate is a bright yellow precipitate, and is used as a pigment under the name of *chrome-yellow*; if boiled with caustic potash or soda it yields *chrome-red* ($PbCrO_4$, PbO), an orange-red pigment.

Tests for Lead.

Wee.

(i) Sulphuretted hydrogen gives a black precipitate of lead sulphide. This is the test employed for the detection of lead in a drinking water, the absence of other metals yielding precipitates with sulphuretted hydrogen being proved; if lead is present in the water, a brownish or blackish colour, according to the amount present, will be produced on the addition of sulphuretted hydrogen.

(ii) Ammonium sulphide also precipitates the black lead sulphide.

(iii) Potassium iodide gives a bright yellow precipitate of lead iodide, soluble in boiling water, and crystallising out in golden-coloured spangles as the solution cools.

(iv) Potassium chromate gives a yellow precipitate of lead chromate, changing to an orange-red colour on boiling with caustic potash or caustic soda.

(v) Hydrochloric acid gives, with moderately strong solutions of lead salts, a white precipitate of lead chloride; this precipitate remains unaltered on the addition of solution of ammonia, thus distinguishing it from mercurous chloride, which is also thrown down as a white precipitate by hydrochloric acid from a solution of a mercurous salt. Hydrochloric acid does not completely precipitate lead from its solutions, as lead chloride is appreciably soluble in cold water, and more so in hot water.

(vi) Sulphuric acid gives with solutions of lead salts a white precipitate of lead sulphate. Sol in acids

(vii) If a solid lead compound be heated on charcoal with Na_2CO_3 a malleable globule of lead is obtained, surrounded by a yellow incrustation.

The metals tin and lead have several points of resemblance; they are both soft, malleable, easily reducible metals. When heated in the air they form oxides. They are bivalent and tetravalent, and form two oxides (SnO, SnO_2) and two chlorides ($SnCl_2$, $SnCl_4$), etc. They belong to the same family of elements as the non-metals, carbon and silicon. The highest oxides of tin and lead show feeble acid properties, but their salts, the stannates and plumbates, are very unstable.

KI
H₂SO₄
white
black

CHAPTER VI.

ARSENIC—ANTIMONY—BISMUTH.

Arsenic—Occurrence in Nature—Arsenious and Arsenic Compounds—Tests for Arsenic—Antimony—Occurrence in Nature—Preparation of the Antimony Salts—Tests for Antimony—Bismuth—Bismuth Salts—Tests for Bismuth.

ARSENIC.

Cf. P4

S4 *Symbol*, As; *molecule*, As$_4$; *pentad and triad; atomic weight*, 75; *molecular weight*, 300; *specific gravity*, 5·7.

ARSENIC and phosphorus are the only elements containing four atoms in the molecule; their molecular weights are, therefore, four times their atomic weights.

Natural compounds of arsenic.—(i) The commonest arsenical ore is mispickel or arsenical iron pyrites (FeSAs). (ii) Two compounds of arsenic and sulphur occur in nature, a yellow sulphide named *orpiment* (As_2S_3), and a red sulphide named *realgar* (As_2S_2). (iii) *Arsenious acid* (H_3AsO_3) occurs in minute amounts in several mineral springs, as in those of Ems, Kissingen, Pyrmont, and Schwalbach. The quantity of arsenious acid present in these waters is too small to confer poisonous properties on them when drunk, but it is quite possible that their therapeutic properties are in part due to the minute quantities of arsenic present. (iv) The *metal arsenic* occurs native to a small extent.

Preparation of the metal arsenic.—The metal arsenic is obtained as a sublimate by passing arsenic = heated.

the vapour of arsenious oxide or white arsenic (As_4O_6) over heated charcoal.

$$\underset{\text{Arsenious oxide.}}{As_4O_6} + \underset{\text{Carbon.}}{6C} = \underset{\text{Arsenic.}}{As_4} + \underset{\text{Carbon monoxide.}}{6CO}$$

Properties of the metal.—Arsenic possesses a steel-grey colour and a metallic lustre; it is very brittle, and is therefore easily pulverised. When heated in the air, arsenic volatilises and burns, forming arsenious oxide or white arsenic (As_4O_6), and emitting at the same time an unpleasant garlic-like odour. Arsenic begins to volatilise at 100°, it passes rapidly into vapour at 180°, and can be melted (500°) only under pressure. The only use to which the metal arsenic is put, is in the manufacture of shot, which consist of lead alloyed with a small amount of arsenic.

COMPOUNDS OF ARSENIC.

Two classes of arsenical compounds exist, viz. the *arsenious compounds*, in which the arsenic is only exerting the atomicity of a triad; and the *arsenic compounds*, in which the arsenic is exerting its full atomicity as a pentad.

There are two oxides of arsenic, arsenious oxide and arsenic oxide, or arsenic pentoxide.

Arsenious oxide (As_4O_6).—This oxide constitutes the *white arsenic* of commerce; it is also known as *arsenious anhydride*. It is obtained during the smelting or roasting of arsenical iron pyrites and other ores containing arsenic united with sulphur, the latter element burning away as sulphur dioxide, whilst the arsenic volatilises and oxidises to arsenious oxide, which is then condensed to a solid in long condensing flues attached to the smelting furnace.

$$\underset{\text{Arsenious sulphide.}}{2As_2S_3} + \underset{\text{Oxygen.}}{9O_2} = \underset{\text{Arsenious oxide.}}{As_4O_6} + \underset{\text{Sulphur dioxide.}}{6SO_2}$$

There are two varieties of arsenious oxide—(*a*) a crystalline variety which can be obtained in small octahedra, and (*b*) a vitreous variety constituting the deposit in the condensing flues attached to the furnaces in which arsenical ores are being roasted; this vitreous variety is obtained at first as a semi-transparent, glass-like solid, becoming after a time opaque, like porcelain. The *white arsenic* of commerce is obtained by grinding this vitreous variety to a powder. Arsenious oxide or white arsenic is a white, odourless, and almost tasteless substance, possessing a very faint sweetish taste; it is very poisonous, 2 to 4 grains being usually a poisonous dose; in cases of poisoning with arsenic the administration of freshly-precipitated ferric hydrate or of solution of dialysed iron will act as an antidote, although not a very efficacious one, by forming the insoluble arseniate of iron. Arsenious oxide or white arsenic is soluble in cold water to the extent of half a grain in a fluid ounce, and in boiling water to the extent of 6 grains in a fluid ounce; when dissolved in water it forms arsenious acid (H_3AsO_3). The specific gravity of the vapour of arsenious oxide is 198, its molecular weight is therefore 198 × 2 = 396, which gives the formula As_4O_6.

Arsenic oxide or **arsenic pentoxide** (As_2O_5).—This, the higher oxide of arsenic, is obtained by the oxidation of arsenious oxide with nitric acid; if ordinary white arsenic be heated with nitric acid, reddish-brown fumes of oxides of nitrogen are evolved, and the residue, if dried and raised to a low red heat to expel water, leaves the arsenic oxide.

Arsenic oxide or arsenic anhydride is a white amorphous substance, dissolving in water to form

N_2O_5 —

arsenic acid (H_3AsO_4); although more soluble in water than arsenious oxide, it is less poisonous than that substance. At temperatures above a red heat arsenic anhydride breaks up into arsenious anhydride and oxygen.

There are two acids of arsenic corresponding to the two oxides or anhydrides, viz. arsenious acid and arsenic acid.

Arsenious acid (H_3AsO_3).—This is prepared by dissolving white arsenic (arsenious anhydride) in water.

$$\underset{\text{Arsenious anhydride.}}{As_4O_6} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Arsenious acid.}}{4H_3AsO_3}$$

It is a weak acid, and is only slightly soluble in water; it is too weak an acid to decompose solutions of the alkaline carbonates; arsenious acid is contained in two solutions used in medicine, both of them containing 1 per cent. of arsenic in solution; these are Fowler's solution (*Liquor arsenicalis*) and the hydrochloric solution of arsenic (*Liquor arsenici hydrochloricus*). Although arsenious acid is so sparingly soluble in cold water, yet it is much more soluble in a dilute solution of an alkaline carbonate, or in a weak mineral acid. On this account Fowler's solution contains some potassium carbonate, which merely increases the solubility of the arsenious acid; and the hydrochloric solution of arsenic contains some diluted hydrochloric acid, which also increases the solubility of arsenious acid.

Two compounds of arsenious acid are not uncommonly employed as pigments, viz. Scheele's green (arsenite of copper) and emerald green (aceto-arsenite of copper).

Scheele's green is prepared by mixing together solutions of copper sulphate and sodium arsenite, when it is thrown down as a bright green precipitate.

$$\underset{\text{Copper sulphate.}}{CuSO_4} + \underset{\text{Sodium arsenite.}}{Na_2HAsO_3} = \underset{\text{Copper arsenite.}}{CuHAsO_3} + \underset{\text{Sodium sulphate.}}{Na_2SO_4}$$

Wall-papers printed with bright green colours are frequently surfaced with Scheele's green or emerald green, the arsenic contained in which may exercise a very injurious influence on people living or sleeping in rooms so papered. The arsenical pigment may become brushed off the paper as dust, and so become disseminated through the atmosphere of the room. But it is not only by this mechanical means that the arsenic can be dispersed into the atmosphere of the room; the papers are fastened to the walls with starch-paste, which easily ferments and sets free nascent hydrogen; and since the paper is originally saturated with the paste, this nascent hydrogen comes directly into contact with the arsenical compounds, and produces gaseous arseniuretted hydrogen, which escapes into and poisons the air of the room. It is true that the quantity of the gas so produced is very minute; but as arseniuretted hydrogen is more poisonous than any other compound of arsenic, very small quantities may be sufficient to produce very injurious effects.

For the methods of detecting arsenic in wall-papers, *see* pages 287, 289.

Arsenic acid (H_3AsO_4).—This is obtained by dissolving arsenic anhydride in water.

$$\underset{\text{Arsenic anhydride.}}{As_2O_5} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Arsenic acid.}}{2H_3AsO_4}$$

It may also be prepared by the action of chlorine on a solution of arsenious acid, the chlorine uniting with the hydrogen of some of the water to form hydrochloric acid, and setting free oxygen, which in the nascent state oxidises the arsenious acid to arsenic acid.

$$\underset{\substack{\text{Arsenious}\\\text{acid.}}}{H_3AsO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Arsenic}\\\text{acid.}}}{H_3AsO_4} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl}$$

A similar action occurs when iodine is added to a solution of arsenious acid.

$$\underset{\substack{\text{Arsenious}\\\text{acid.}}}{H_3AsO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Iodine.}}{I_2} = \underset{\substack{\text{Arsenic}\\\text{acid.}}}{H_3AsO_4} + \underset{\substack{\text{Hydriodic}\\\text{acid.}}}{2HI}$$

Arsenic acid is a stronger acid as regards its action on litmus paper, and its power of forming salts, than arsenious acid, and is much more soluble in water, but it is not so powerful a poison as arsenious acid. Arsenic acid is employed in the preparation of magenta and some other aniline dyes, becoming reduced to arsenious acid during the process. If the dye is not properly freed from the arsenious acid, then injurious effects may follow from the employment of articles coloured with such dyes, such as socks, gloves, Cretonne and other hangings. Red aniline dyes are also sometimes used for giving a colour to liqueurs, syrups, sweetmeats, and raspberry vinegar; and here, again, injurious effects might follow from the taking of such coloured articles if the dye contained arsenic. A potassium arseniate (K_2HAsO_4) is contained in some fly-papers, flies being readily killed by imbibing a small quantity of a solution of this salt.

Two salts of arsenic acid are used in medicine, viz. sodium arseniate (*see* page 227) and ferrous arseniate (*see* Iron salts).

Arsenious chloride ($AsCl_3$) is prepared by burning powdered arsenic in dry chlorine, or by distilling a mixture of arsenious anhydride, sodium chloride, and concentrated sulphuric acid. It is a colourless volatile liquid, decomposed by water into arsenious and hydrochloric acids.

$AsCl_3$	+	$3H_2O$	=	H_3AsO_3	+	$3HCl$
Arsenious chloride.		Water.		Arsenious acid.		Hydrochloric acid.

Arsenious iodide (AsI_3) is prepared by direct union of its elements or by dissolving arsenious anhydride in hydriodic acid. An aqueous solution, containing 1 per cent. of this arsenious iodide and 1 per cent. of mercuric iodide, with an excess of potassium iodide, forms Donovan's solution (*Liquor arsenii et hydrargyri iodidi*, B. P.).

Tests for Arsenic.

(i) Sulphuretted hydrogen gives, with an acid solution of arsenious acid, a yellow precipitate of arsenious sulphide, which is soluble in alkalies and in ammonium sulphide.

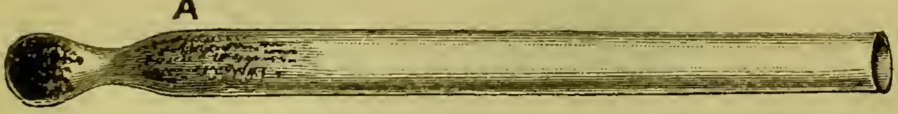


Fig. 25.—Sublimate of Metallic Arsenic in a Berzelius's Reduction Tube.

(ii) If a small quantity of white arsenic is mixed with a reducing agent containing carbon, such as *black flux* (a mixture of potassium carbonate and charcoal, obtained by heating acid tartrate of potassium in a covered vessel), and the mixture introduced into a Berzelius's reduction tube, and then heat applied to the bulb containing the mixture, a sublimate of metallic arsenic of an iron-grey colour will be obtained on the cool part of the tube just above the constriction. (Fig. 25, A being the sublimate of the metallic arsenic.)

If the portion of the tube containing the sublimate A be cut off with a file, and then broken into fragments, and the fragments introduced into a dry test-tube, on applying heat to the bottom of the latter, whilst holding it in an almost horizontal position, with the mouth of the tube partially covered by the thumb, the arsenic will volatilise and oxidise to arsenious oxide, which will deposit on the cool part of the tube in small brilliant crystals, consisting of perfect and imperfect octahedra. If the portion of the tube containing the sublimate be viewed under a microscope, using a $\frac{1}{4}$-in. or $\frac{1}{5}$-in. objective, the crystals will present the characteristic appearances shown in Fig. 26.

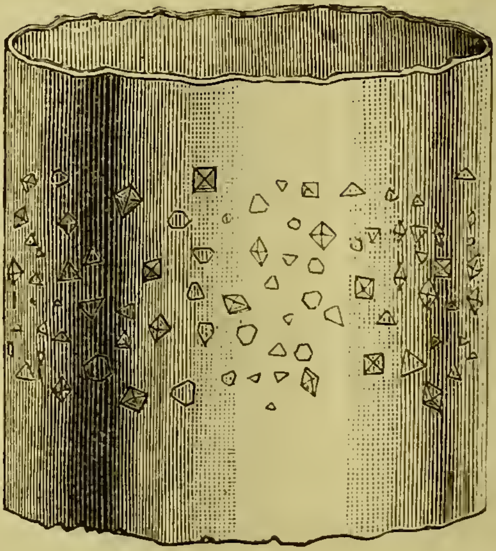


Fig. 26.—Crystals of Arsenious Oxide (magnified).

(iii) *Reinsch's test.*—This very delicate test for arsenic consists in boiling, for a short time, a strip of bright copper foil in a solution of arsenious acid, to which one-sixth its volume of hydrochloric acid has been added. The metal arsenic deposits on the surface of the copper as a dull grey film. The acid liquid is then poured off from the slip of copper, and the latter washed two or three times with water and dried, firstly by pressure between folds of blotting-paper, and lastly by carefully warming it some distance above the Bunsen flame. The strip of copper, with the deposit of arsenic on it, is now transferred to a dry test-tube, and heat is applied in a manner similar to that described in the previous test, when the arsenic volatilises and oxidises to arsenious oxide, which forms a crystalline deposit on the cool part of the tube, presenting under the microscope the characteristic appearances shown in Fig. 26.

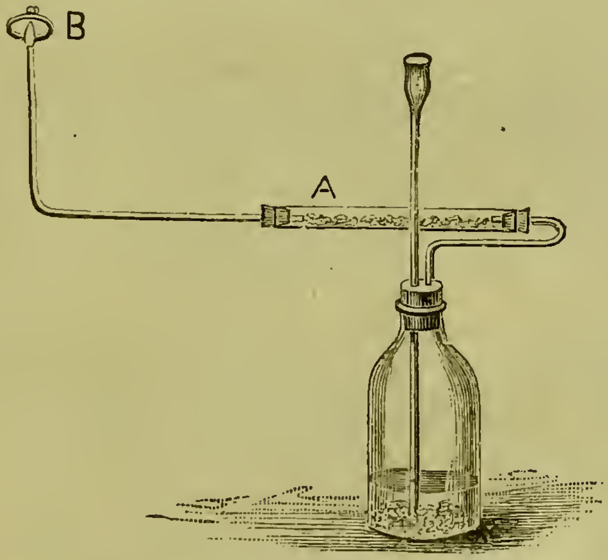


Fig. 27.—Apparatus for Marsh's Test.

Reinsch's test may be employed for the detection of arsenic in wall-paper. Some of the paper is cut into small pieces, which are then digested in diluted hydrochloric acid with heat for a few minutes; the acid liquid is poured off, boiled with a strip of bright copper, and the test proceeded with in the manner just described.

iv. *Marsh's test.*—This delicate test for arsenic depends upon the conversion of the arsenic into arseniuretted hydrogen, and obtaining from the latter a deposit of metallic arsenic. Hydrogen is generated in a suitable apparatus (Fig. 27) from pure zinc and dilute sulphuric acid; the gas is dried by passing through a calcium chloride tube (A in Fig. 27), and is then ignited as it escapes from the end of the tube bent at right angles.

If some solution of arsenious acid is now poured into the apparatus by means of the long funnel, the nascent hydrogen produces arseniuretted hydrogen (AsH_3), the production of which is quickly indicated by the hydrogen flame becoming a pale livid colour.

$$\underset{\substack{\text{Arsenious}\\ \text{acid.}}}{H_3AsO_3} + \underset{\text{Hydrogen.}}{3H_2} = \underset{\substack{\text{Arseniuretted}\\ \text{hydrogen.}}}{AsH_3} + \underset{\text{Water.}}{3H_2O}$$

In arseniuretted hydrogen the two elements are so loosely combined that a low red-heat is sufficient to decompose the compound into metallic arsenic and hydrogen; the gas, therefore, when passed through a glass tube, the central portion of which is made red-hot, deposits a mirror of metallic arsenic on the cooler parts of the tube just beyond the heated portion. The same decomposition is taking place when arseniuretted hydrogen is inflamed in the air; the high temperature of the flame decomposes the unburnt gas in the interior of the flame into arsenic and hydrogen, and it is this finely-divided metallic arsenic which imparts to the flame its pale livid colour. The presence of this metallic arsenic in the interior of the flame is readily proved, and constitutes the final stage of Marsh's test; for if a piece of cold white porcelain, such as an evaporating dish or porcelain crucible lid (B in Fig. 27), is pressed down upon the flame for a moment or two, the cold porcelain becomes coated with a round blackish-grey stain of metallic arsenic at the spot where the flame touched it. This spot of metallic arsenic readily dissolves in

Sod. hypo chlorite
NaOCl.

solution of chlorinated lime or chlorinated soda, and so can be distinguished from the antimony spot, which is obtained under similar conditions (*see* page 294). To detect arsenic in wall-paper by means of Marsh's test, it is simply necessary to introduce into Marsh's apparatus some of the acid liquid obtained by digesting pieces of the paper in diluted hydrochloric acid with heat, the test being then proceeded with in the usual way.

In employing Marsh's test, care must be taken that no unburnt arseniuretted hydrogen escapes into the atmosphere of the laboratory, as it is a most powerful poison, being, in fact, more poisonous than any other arsenical compound.

(v) If to an aqueous solution of arsenious acid some copper sulphate be added, and then a drop or two of solution of ammonia, a bright green precipitate (Scheele's green) will be thrown down.

(vi) If to an aqueous solution of arsenious acid some silver nitrate be added, and then a drop or two of dilute solution of ammonia, a bright yellow precipitate of silver arsenite will be obtained. This reaction may be applied to the detection of arsenic in wall paper; about a square inch of the paper, with the coloured surface uppermost, is placed in a small porcelain dish, distilled water is poured on so as just to cover the paper, and a few drops of solution of ammonia are added; after standing for a minute or two, a crystal of silver nitrate is dropped into the dish on to the surface of the piece of paper, when, if arsenic be present, a yellow deposit of silver arsenite will occur around the edge and over the surface of the crystal. This test depends upon the solubility of Scheele's green (copper arsenite) in a weak solution of ammonia, and the precipitation from this solution of the yellow silver arsenite, in presence of an excess of silver nitrate.

$AgNO_3$ < yellow—ous & ites

Distinction between Arsenious and Arsenic Acids.

If to an aqueous solution of arsenic acid some silver nitrate be added, and then a drop or two of solution of ammonia, a *chocolate-coloured* precipitate of silver arseniate will be obtained; this test serves to distinguish between the two acids, as in similar circumstances arsenious acid will give a *bright yellow* precipitate. In like manner, neutral solutions of arseniates will at once give a chocolate precipitate, and neutral solutions of arsenites a yellow precipitate, with silver nitrate.

ANTIMONY.

Symbol, Sb; *pentad and triad*; *atomic weight*, 120·4; *specific gravity*, 6·6; *melts*, 629°.

Natural compounds of antimony.—The sulphide of antimony (Sb_2S_3) is the principal natural compound of this metal; it is known as *grey antimony ore*, and in the form of powder as *black antimony*.

Preparation and properties of the metal antimony.—This is obtained by heating together the native sulphide of antimony and metallic iron, the iron uniting with the sulphur to form ferrous sulphide, and setting free the antimony.

$$\underset{\text{Antimony sulphide.}}{Sb_2S_3} + \underset{\text{Iron.}}{3Fe} = \underset{\text{Antimony.}}{2Sb} + \underset{\text{Ferrous sulphide.}}{3FeS}$$

Crude antimony contains arsenic, from which it can be purified by fusing with some sodium carbonate and potassium nitrate, and well stirring the mixture, when the arsenic becomes converted into sodium arseniate.

Antimony is a hard, brittle, white metal; when heated before the blowpipe it burns, giving a white vapour of the oxide; it is contained in *type-metal*, an alloy of lead and antimony and tin, and in *britannia-metal,* an alloy of tin and antimony.

Antimony trioxide or **antimonious oxide** (Sb_2O_3) is prepared by pouring the acid solution of antimony trichloride into water, by which means a white precipitate of oxychloride of antimony is thrown down.

$$\underset{\text{Antimony trichloride.}}{12SbCl_3} + \underset{\text{Water.}}{15H_2O} = \underset{\text{Antimony oxychloride.}}{2SbCl_3, 5Sb_2O_3} + \underset{\text{Hydrochloric acid.}}{30HCl}$$

This precipitate is then stirred up with solution of sodium carbonate, which abstracts the chlorine from the oxychloride, producing the pure antimony trioxide, which is of a light buff colour.

$$\underset{\text{Antimony oxychloride.}}{2SbCl_3, 5Sb_2O_3} + \underset{\text{Sodium carbonate.}}{3Na_2CO_3} = \underset{\text{Antimony trioxide.}}{6Sb_2O_3} + \underset{\text{Sodium chloride.}}{6NaCl} + \underset{\text{Carbon dioxide.}}{3CO_2}$$

Antimony pentoxide or **antimonic oxide** (Sb_2O_5) is prepared by the action of nitric acid on the metal antimony.

Antimony Salts.

There are two classes of antimony compounds, the *antimonious* and *antimonic*, resembling the two classes of arsenical compounds; in the antimonious compounds the antimony is only exerting part of its atomicity as a triad, whereas in the antimonic compounds it is exerting its full atomicity as a pentad.

Antimony trichloride or **antimonious chloride** ($SbCl_3$).—(1) This may be prepared by direct union of the elements; if powdered metallic antimony is thrown into a jar of chlorine, it will catch fire, producing antimony trichloride.

$$\underset{\text{Antimony.}}{2Sb} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\substack{\text{Antimony}\\\text{trichloride.}}}{2SbCl_3}$$

(ii) The usual method of preparing this chloride is by the action of strong hydrochloric acid with heat on the native sulphide of antimony.

$$\underset{\substack{\text{Antimony}\\\text{sulphide.}}}{Sb_2S_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6HCl} = \underset{\substack{\text{Antimony}\\\text{trichloride.}}}{2SbCl_3} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{3H_2S}$$

Prepared in this way it is generally of a reddish-brown colour from the presence of iron salts; it is a strongly acid liquid, commonly known as *butter of antimony*, but it is actually a solution of antimony trichloride in hydrochloric acid, since the chloride itself is of a buttery consistence, whence its common name. The true butter of antimony is obtained by evaporating the acid solution to a low bulk, and distilling the residue, when the antimony trichloride condenses in the neck of the retort as a white, semi-transparent mass.

Antimony pentachloride or **antimonic chloride** ($SbCl_5$) is prepared by acting on the trichloride with chlorine.

$$\underset{\substack{\text{Antimony}\\\text{trichloride.}}}{SbCl_3} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Antimony}\\\text{pentachloride.}}}{SbCl_5}$$

Tartarated antimony ($KSbOC_4H_4O_6$).—This compound, commonly known as *tartar emetic*, is a tartrate of potassium and antimony. It is prepared by mixing antimony trioxide and potassium acid tartrate with sufficient water to form a paste, leaving it for twenty-four hours, as the two substances are somewhat sluggish in uniting, and then boiling the paste with water; on filtering, and concentrating the solution by evaporation, the tartar emetic is obtained in crystals, which contain a half molecule of water of crystallisation.

$$\underset{\text{Antimony trioxide.}}{Sb_2O_3} + \underset{\text{Potassium acid tartrate.}}{2KHC_4H_4O_6} = \underset{\text{Tartar emetic.}}{2KSbOC_4H_4O_6} + \underset{\text{Water.}}{H_2O}$$

It will be noticed in this compound that one of the hydrogen atoms of the tartaric acid is replaced by the metal potassium, and the other, not by the *metal* antimony, but by the univalent radicle (—Sb=O).

Sulphurated antimony.—Prepared by boiling native black sulphide of antimony and sulphur with solution of caustic soda, filtering and precipitating the sulphurated antimony with diluted sulphuric acid, when it is thrown down as an orange-red precipitate. It is a mixture of the sulphides and oxides of antimony, and is one of the many varieties of *mineral kermes*, so called from their similarity in colour to the *insect kermes*; *kermes* being the old name of the cochineal insect.

Tests for Antimony.

(i) Hydrochloric acid gives, with a neutral solution of an antimony salt (such as tartar emetic), a white precipitate of oxychloride of antimony, soluble in excess of hydrochloric acid; if this solution be poured into water the oxychloride is again precipitated.

(ii) Sulphuretted hydrogen gives, with an acid solution of an antimony salt, an orange-red precipitate of antimony sulphide (Sb_2S_3), soluble in alkalies and in ammonium sulphide.

(iii) If a solution of an antimony salt, to which sufficient hydrochloric acid is added to dissolve any precipitate at first thrown down, be boiled with a strip of bright copper foil, a dark grey film of metallic antimony will be deposited on the copper; if the strip of copper be now treated in a manner precisely similar to that described in connection with Reinsch's test for arsenic (*see* page 286), a white sublimate of antimony oxide will be obtained, but differing from the arsenic sublimate in that it is amorphous, and that it is deposited on the sides of the tube much nearer to the copper than the arsenic sublimate, on account of the antimony being less volatile than arsenic.

(iv) If the operations described under Marsh's test for arsenic (*see* page 287) be repeated, substituting an antimony salt for an arsenical compound, then antimoniuretted hydrogen (SbH_3) will be evolved; antimoniuretted hydrogen communicates a livid colour to the burning hydrogen flame, and is decomposed like arseniuretted hydrogen at a low red heat, a black spot of metallic antimony being obtained on a cool porcelain dish or crucible lid introduced for a moment into the flame. As previously mentioned, this antimony spot can be distinguished from the arsenic spot obtained in similar circumstances by being insoluble in solution of chlorinated lime or chlorinated soda, whereas the arsenic spot readily dissolves in either of these solutions.

(v) If a solid antimony compound be heated on charcoal with sodium carbonate, a brittle metallic globule of antimony is obtained surrounded by a white incrustation.

105° Use as a safety plug for [illegible] [illegible]
boilers [illegible] [illegible] [illegible] 105 [illegible] steam
mills

BISMUTH.

Symbol, Bi; *triad; atomic weight*, 208·1; *specific gravity*, 9 9; *melts at* 264°.

Occurrence in nature.—Bismuth occurs in the metallic state in nature, mixed with quartz and other earthy substances; it is separated by melting it away from these impurities. Bismuth obtained in this way is generally contaminated with variable quantities of the metal arsenic, from which it may be purified by melting it with potassium nitrate, and well stirring the mixture, when the arsenic is oxidised to potassium arseniate. Bismuth is a hard brittle metal with a reddish tinge. ~~Hydrochloric and sulphuric acids do not~~ act upon it in the cold. Nitric acid dissolves it readily. It forms various fusible alloys, the most useful of which is *Wood's metal*, which contains 4 parts by weight of bismuth, 2 of lead, 1 of tin, and 1 of cadmium; it melts at 61°, and is very useful for taking casts; it is quite hard when cold.

Bismuth oxide (Bi_2O_3) is prepared by boiling bismuth oxynitrate with solution of caustic soda; it is a yellow powder.

$$\underset{\text{Bismuth oxynitrate.}}{2BiONO_3} + \underset{\text{Sodium hydrate.}}{2NaHO} = \underset{\text{Bismuth oxide.}}{Bi_2O_3} + \underset{\text{Sodium nitrate.}}{2NaNO_3} + \underset{\text{Water.}}{H_2O}$$

BISMUTH SALTS.

Bismuth nitrate ($Bi(NO_3)_3$) is prepared by the action of strong nitric acid on bismuth.

$$\underset{\text{Bismuth.}}{Bi} + \underset{\text{Nitric acid.}}{4HNO_3} = \underset{\text{Bismuth nitrate.}}{Bi(NO_3)_3} + \underset{\text{Nitrogen dioxide.}}{NO} + \underset{\text{Water.}}{2H_2O}$$

Bismuth oxynitrate ($BiONO_3 + 5H_2O$).—This compound is derived from bismuth nitrate, by the displacement of two univalent nitric radicles by the dyad oxygen; it is prepared by pouring bismuth nitrate into water, when it is thrown down as a white precipitate.

$$\underset{\text{Bismuth nitrate.}}{Bi(NO_3)_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Bismuth oxynitrate.}}{BiONO_3} + \underset{\text{Nitric acid.}}{2HNO_3}$$

It is largely used in medicine under the name of subnitrate of bismuth (*Bismuthi subnitras*); it is also employed as a cosmetic or face-powder under the name of *Pearl white* (Blanc de Perle).

Bismuth oxycarbonate ($(Bi_2O_2CO_3)_2 + H_2O$).—This compound may be regarded as bismuth oxide (Bi_2O_3), from which one atom of oxygen is displaced by an equivalent quantity of the dyad carbonic radicle. It is prepared by pouring bismuth nitrate into a solution of ammonium carbonate.

$$\underset{\text{Bismuth nitrate.}}{2Bi(NO_3)_3} + \underset{\text{Ammonium carbonate.}}{3(NH_4)_2CO_3} = \underset{\text{Bismuth oxycarbonate.}}{Bi_2O_2CO_3} + \underset{\text{Ammonium nitrate.}}{6NH_4NO_3} + \underset{\text{Carbon dioxide.}}{2CO_2}$$

This compound is also extensively used in medicine under the name of carbonate of bismuth (*Bismuthi carbonas*).

Tests for Bismuth.

(1) If any acid salt of bismuth is concentrated and then poured into an excess of water, a white oxysalt is precipitated.

Bi

(ii) Hydrochloric acid added to a neutral solution of a bismuth salt gives a white precipitate of bismuth oxychloride, soluble in excess of hydrochloric acid. The only other metal yielding a white precipitate with hydrochloric acid, soluble in excess of the acid, is antimony; the two metals can be readily distinguished by the different colours of their sulphides, as precipitated by sulphuretted hydrogen, the sulphide of bismuth being black and the sulphide of antimony orange red. The oxychloride of antimony is also soluble in tartaric acid, in which the corresponding bismuth compound is insoluble.

(iii) Sulphuretted hydrogen gives with bismuth salts a brownish-black precipitate of bismuth sulphide.

(iv) If a solid compound of bismuth be heated on charcoal with sodium carbonate, a brittle bead of bismuth is obtained surrounded with an orange incrustation.

The metals arsenic, antimony and bismuth have many points of analogy with the non-metals nitrogen and phosphorus. They are all triads and pentads. Arsenic and antimony form compounds with hydrogen AsH_3 and SbH_3, which are gases having strong odours, just as nitrogen and phosphorus form ammonia and phosphine. Arsenic, antimony and bismuth are all brittle metals. They form two principal oxides, As_2O_3, As_2O_5, etc., and, as in the last family (page 278), the acid character of the oxides decreases as the atomic weight of the element rises. The arsenates crystallise in the same form as the corresponding phosphates, and both these salts give a crystalline precipitate with magnesium sulphate in the presence of ammonium salts.

S | An S
HNO_3 [illegible]
KCN [illegible]
NaOH white [illegible] + blackening with [illegible]
water - white

CHAPTER VII.

CHROMIUM—MANGANESE—IRON—COBALT—NICKEL.

Chromium—Chromium Compounds—Tests for Chromium—Manganese—Manganese Compounds—Tests for Manganese—Iron—Natural Compounds of Iron—Preparation and Properties of the Metal Iron—Cast Iron—Wrought Iron—Steel—Action of Acids on Iron—Preparation of the Ferrous and Ferric Salts—Tests for Iron—Distinguishing Tests between Ferrous and Ferric Salts—Cobalt—Nickel.

CHROMIUM.

Symbol, Cr.; *hexad; atomic weight*, 52·2; *specific gravity*, 6·29.

The principal compound of chromium occurring in nature is *chrome iron ore* (FeO, Cr_2O_3).

Chromium is a white metal prepared by heating chromic oxide with carbon in the electric furnace; it is very infusible.

Potassium chromate (K_2CrO_4).—This compound, known also as *yellow chromate of potash*, is prepared from chrome iron ore by fusing it with potassium carbonate and potassium nitrate; ferric oxide and potassium chromate result, the latter being dissolved out by boiling the fused mass with water.

Potassium dichromate (K_2CrO_4,CrO_3).—This is more commonly called *bichromate of potash* or, on account of its colour, *red chromate of potash.* It is prepared by adding to a solution of potassium chromate the theoretical quantity of sulphuric acid, when the dichromate crystallises out on cooling.

$$\underset{\substack{\text{Potassium}\\\text{chromate.}}}{2K_2CrO_4} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} = \underset{\substack{\text{Potassium}\\\text{dichromate.}}}{K_2Cr_2O_7} + \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4} + \underset{\text{Water.}}{H_2O}$$

Chromic oxide (Cr_2O_3).—Green oxide of chromium may be prepared by strongly heating ammonium dichromate.

Chromic anhydride (CrO_3).—Red oxide of chromium is obtained by mixing together two volumes of a saturated solution of potassium dichromate and three volumes of strong sulphuric acid; as the mixture cools, the chromic anhydride crystallises out in long slender needles of a bright crimson colour.

$$\underset{\substack{\text{Potassium}\\\text{dichromate.}}}{K_2CrO_4,CrO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Chromic}\\\text{anhydride.}}}{2CrO_3} + \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4} + \underset{\text{Water.}}{H_2O}$$

Chromic anhydride is used as a powerful caustic under the name of chromic acid (*Acidum chromicum*); it is the anhydride of chromic acid, into which it is converted by dissolving in water.

$$\underset{\substack{\text{Chromic}\\\text{anhydride.}}}{CrO_3} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Chromic}\\\text{acid.}}}{H_2CrO_4}$$

Solutions of chromic acid and potassium bichromate are much used for hardening tissues for histological purposes. A solution of gelatin containing 10 per cent. of potassium bichromate becomes, after exposure to light, insoluble in hot water.

Chrome alum ($Cr_2(SO_4)_3,K_2SO_4 + 24H_2O$).—This is prepared by heating potassium dichromate with sulphuric acid in presence of some reducing agent such as alcohol, sulphur dioxide, hydrogen sulphide, nascent hydrogen, etc.

$$\underset{\text{Potassium bichromate.}}{K_2Cr_2O_7} + \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Sulphur dioxide.}}{3SO_2} + \underset{\text{Water.}}{23H_2O} =$$

$$\underbrace{Cr_2(SO_4)_3 + K_2SO_4}_{\text{Chrome alum.}} + 24H_2O$$

Tests for Chromium.

If a chromium salt be fused with sodium carbonate and potassium nitrate on a piece of platinum foil, the yellow sodium chromate is formed; on dissolving this in boiling water, and acidifying the solution with acetic acid, a yellow precipitate (lead chromate) will be obtained on the addition of lead acetate.

If a solid chromium compound be fused into a borax bead, the latter is coloured green.

MANGANESE.

Symbol, Mn; *hexad*; *atomic weight*, 55.

The chief natural compound of manganese is the *black oxide of manganese* or *pyrolusite* (MnO_2). Manganese exerts its full atomicity as a hexad in the manganates and permanganates; in the black oxide of manganese it only exerts the atomicity of a tetrad, whilst in manganous sulphate ($MnSO_4$) and manganous chloride it acts as a dyad only. The metal is added to Bessemer steel to improve its quality.

Manganous sulphate ($MnSO_4 + 7H_2O$).—When manganese dioxide is heated with strong sulphuric acid, oxygen is evolved and manganous sulphate produced.

$$\underset{\text{Manganese dioxide.}}{2MnO_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Manganous sulphate.}}{2MnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{O_2}$$

Manganous chloride ($MnCl_2$).—This compound is obtained as a by-product in the preparation manganous salt are pale pink

of chlorine from manganese dioxide and hydrochloric acid (*see* page 128). The manganous salts are pale pink.

Potassium manganate and **permanganate.**—The latter of these compounds is the most important manganese preparation, from the medical point of view. (For their preparation and properties, *see* pages 218, 219.)

Tests for Manganese.

(i) Ammonium sulphide throws down a flesh-coloured precipitate of manganous sulphide.

(ii) Solution of ammonia gives a white precipitate of manganous hydrate, which darkens on exposure to the air, owing to absorption of oxygen and conversion into the black oxide of manganese.

(iii) If a manganese salt is fused with sodium carbonate and potassium nitrate on a piece of platinum foil, the green sodium manganate is obtained; if this be boiled with water, a red solution is obtained, owing to the conversion of the manganate into the permanganate.

(iv) If a manganese compound be fused into a borax bead, the latter is coloured amethyst in the outer, but remains colourless in the inner flame.

IRON.

Symbol, Fe; *triad and dyad; atomic weight*, 56; *specific gravity*, 7·8 to 8·1.

Natural compounds of iron.—(i) The important ore *red hæmatite* consists of ferric oxide (Fe_2O_3); *brown hæmatite* is a ferric oxyhydrate. (ii) *Magnetic iron ore* or *loadstone* consists of ferroso-ferric oxide (FeO,Fe_2O_3). (iii) *Spathic iron ore* is an impure ferrous carbonate ($FeCO_3$); it is found in England mixed with clay, and constitutes *clay iron-*

stone. (iv) Iron occurs to a small extent in the free state in nature in the form of meteorites, which are masses of iron that have fallen on to the earth's surface from extra-terrestrial space. (v) Iron also occurs largely in iron pyrites (FeS_2), but this is not used as an iron ore.

Before studying the preparation of metallic iron from its ores it will be advantageous to state shortly the enormous influence that comparatively small doses of carbon exert on the physical and chemical properties of iron.

Wrought iron contains less than 0·2 per cent. of carbon, it is extremely malleable, infusible in any ordinary furnace, very tough, and when made white hot it becomes pasty, so that two pieces when brought together white hot and hammered can be *welded* together.

Steel contains from 0·3 to 1·4 per cent. of carbon, is malleable, can be fused in a furnace with a good draught, and can be welded; but its most important property is that it can be *tempered*, *i.e.* its hardness can be altered by the rate at which it is cooled; if, for instance, when red hot it is plunged into cold water, it is hard enough to scratch glass, but is very brittle; if, on the other hand, it be allowed to cool gradually it is almost as soft and malleable as wrought iron.

Cast iron contains from 2 to 5 per cent. of carbon, it is comparatively hard and brittle, easily fusible, and cannot be welded. If it is cooled quickly its fracture is usually white, if it is cooled slowly some of the carbon separates as grey particles of graphite.

Cast iron is obtained by first smelting or roasting the iron ore in air, in order to completely convert it into ferric oxide, and then reducing the oxide to the metallic state by strongly heating with coke or coal in presence of some limestone; this reduction of the ferric oxide requires a very high temperature, and is

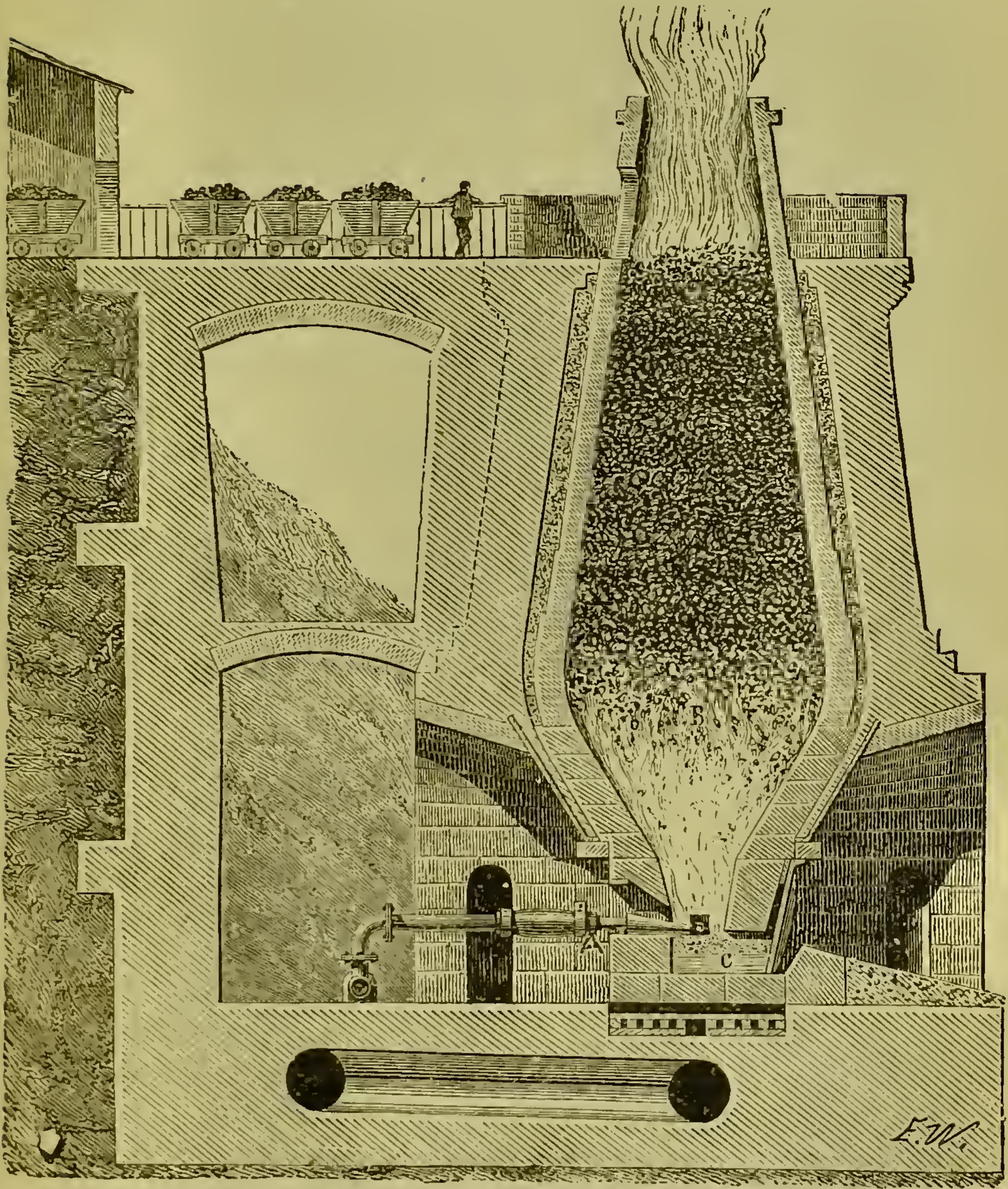


Fig. 28.—Section of a Blast Furnace.

carried out in the *blast-furnace* (Fig. 28). This furnace is constructed of very solid masonry lined with firebricks, and reaches from 60 to 80 feet in height; it is fed from the top, alternate layers of roasted iron ore mixed with limestone and coke or coal being shot in from trucks.

The furnace is supplied at the lower part with a powerful blast of air forced through pipes called tuyères, one of which is shown in the figure at A; this air is heated previous to being forced into the furnace, the hot gases from the top of the furnace being employed for this purpose; to prevent the escape of these gases a cap or hood (not shown in the figure) is placed over the top of the furnace, the gases being conducted by pipes issuing from near the top of the furnace to a chamber through which the pipes conveying the blast of air circulate; by thus using a blast of heated air a much higher temperature is obtained within the furnace. Some of the carbon burns to form carbon dioxide, which with the remaining red-hot carbon produces carbon monoxide, a very powerful reducing agent, and this gas in its passage over the lumps of heated ferric oxide abstracts the oxygen, forming carbon dioxide, and setting free the metal.

$$\underset{\text{Ferric oxide.}}{Fe_2O_3} + \underset{\text{Carbon monoxide}}{3CO} = \underset{\text{Iron.}}{2Fe} + \underset{\text{Carbon dioxide.}}{3CO_2}$$

The metal iron, in a soft or spongy condition, gradually settles down towards the bottom of the furnace; when it arrives at the hottest part (B in figure), it takes up from 4 to 5 per cent. of the carbon, melts, and then accumulates in the molten state at the bottom of the furnace (C in figure). The function of the limestone is to combine with impurities originally present in the iron ore (mainly silica and phosphates), which it does by forming a fusible silicate of calcium and alumina, or *slag*, and so prevents the silica and phosphates from interfering with the running together of the melted cast iron. This fusible slag also trickles down towards the base of the furnace, but being much lighter than the molten iron, it floats on the top of it, and flows out through a suitable opening in the side of the furnace. At the base of the furnace the molten cast iron is run out from time to time through an opening which is temporarily blocked up with clay; it is run into channels made in sand, and solidifies into bars technically known as *pig-iron.* If cast iron be treated with diluted sulphuric or hydrochloric acid, the iron will dissolve in the acid with evolution of hydrogen, and the minute crystals of graphite will be left insoluble, whilst the carbon combined with the iron, as carbide of iron, will unite with some of the escaping hydrogen and form hydrocarbon gases possessing a peculiar and rather disagreeable odour.

Wrought iron is prepared by burning out the carbon from cast iron, which can be effected by melting the cast iron in the bed of a reverberatory furnace, and then, while a current of hot air is passing over the surface of the molten iron, well stirring or *puddling* it so as to freely expose it to the action of the oxygen; in this way the carbon of the cast iron is gradually burnt out, and as the less easily fusible wrought iron is produced, the metal assumes a pasty condition. As the wrought iron is formed it is taken out in lumps, which after hammering are rolled out. During this process, known as the "puddling process," the iron loses sulphur and phosphorus as well as carbon, and so is much improved in toughness.

Steel is intermediate in composition between cast iron and wrought iron, and it is obvious that it may be prepared (*a*) by abstracting part of the carbon from cast iron, till the percentage of carbon is reduced sufficiently; (*b*) by the addition of carbon to wrought iron, so as to raise the percentage; (*c*) by mixing cast iron and wrought iron in such proportions that the mixture shall contain 0·3 to 1·4 per cent. of carbon. These are the three methods actually employed, the first being known as the Bessemer process, the second the old or Cementation process, and the third the Siemens-Martin process.

(*a*) *Bessemer process.*—This consists in burning out the carbon in cast iron, by passing a current of air through melted cast iron. The Bessemer converter consists of a large egg-shaped vessel lined with powdered flint and provided with openings at the base, through which a current of air can be forced; molten cast iron is run in, and the air passed through it, the oxygen of the air rapidly burning away most of the carbon; enough "spiegeleisen" (a variety of cast iron containing manganese) is then added to impart the necessary amount of carbon and manganese, a small quantity of the latter element notably improving the quality of the steel. It is almost impossible to estimate the value of this process, it has practically given us a new material, in cheap steel. In 1856, when the Bessemer process was first used, steel cost £50 a ton, now it can be made for £6 a ton. The original Bessemer process suffered from the defect that as the lining of the converter was silica, an *acid* oxide, all the phosphorus in the cast iron passed into the steel, necessitating, therefore, the use of a cast iron free from phosphorus. This defect has been completely overcome by Thomas and Gilchrist, who substituted a *basic* oxide (a mixture of lime and magnesia) for the powdered flints. The phosphorus combines with the basic lining and passes into the slag, which is sold as a manure, leaving the steel free from this fatal impurity.

(*b*) *Cementation process.*—In this, the old process for producing steel, carbon is added to wrought iron. It is carried out by embedding bars of wrought iron in charcoal powder, and then heating to bright redness for some days; carbon is gradually taken up by the wrought iron, probably by some process of diffusion, and steel is produced—the product is known as *blister steel;* this is melted to distribute the carbon more equally and is then known as *cast steel.*

(*c*) *Siemens-Martin process.* — This consists in fusing cast iron, and then adding to it wrought iron and a small quantity of "spiegeleisen," until the percentage of carbon is brought from 0·3 to 1·4.

Properties of the metal iron.—*Cast iron* has a grey colour, and a crystalline or granular structure; as previously mentioned, its carbon exists partly in the form of minute crystals of graphite disseminated through the mass of the iron, and partly in union with some of the iron as a carbide of iron. Cast iron melts at a lower temperature than any other form of iron.

Wrought iron is fibrous in structure, and therefore much stronger than the crystalline or granular cast iron, but the fibrous texture is apt to undergo a change into the granular condition when exposed to long-continued vibration. All forms of iron are rendered extremely brittle by the presence of silicon, sulphur, or phosphorus, hence the importance of removing these impurities in the slag during the preparation of iron in the blast furnace. Pieces of wrought iron can be welded or joined together by bringing their clean surfaces in contact at a red heat and then hammering them; to clean their surfaces from the film of oxide of iron, which is produced by the action of the air on the heated iron, the blacksmith uses some sand as a flux previous to hammering; the silica uniting with the oxide of iron forms a fusible silicate of iron, which is squeezed out during the process of hammering, and so allows the absolutely clean metallic surfaces to come into contact and unite.

Steel is of a pale grey colour, and capable of taking a high polish; it is finely granular, not fibrous in structure. *Hard steel* is prepared by heating steel to redness, and then rapidly cooling it by immersion in water; it is very brittle and highly elastic. To toughen or *temper* steel, it is gently re-heated, and when the desired temperature is reached, again rapidly cooled.

Reduced iron is pure iron in the form of powder, obtained by passing a stream of hydrogen over heated ferric oxide; the oxygen is abstracted as water, and the iron is left in a finely divided state. It contains about 75 per cent. of metallic iron; the rest is chiefly oxide.

$$\underset{\text{Ferric oxide.}}{Fe_2O_3} + \underset{\text{Hydrogen.}}{3H_2} = \underset{\text{Iron.}}{2Fe} + \underset{\text{Water.}}{3H_2O}$$

All kinds of iron are magnetic—that is, capable of being attracted to and picked up by a magnet, and also capable of being magnetised; soft iron readily becomes magnetised when in contact with a magnet, but loses its magnetism when withdrawn from the magnet, whereas hard steel becomes magnetised very slowly, but when once magnetised, retains its magnetism for a long period.

Iron remains unchanged in dry air or oxygen at ordinary temperatures, but in moist air it readily unites with oxygen and moisture, forming reddish-brown *rust*, a ferric oxyhydrate. At a red-heat, iron is more rapidly oxidised than by moist air at ordinary temperatures, as is well seen in the production of the forge-scales that collect around the blacksmith's anvil, which consist of the black magnetic oxide of iron.

Barff's process for the prevention of rusting of iron consists in coating the iron article with a film of the hard black magnetic oxide (ferroso-ferric oxide), which effectually prevents further oxidation in damp air; to effect this a current of steam is passed for a few minutes over the iron article raised to a red-heat.

$$\underset{\text{Iron.}}{3\mathrm{Fe}} + \underset{\text{Water.}}{4\mathrm{H_2O}} = \underset{\substack{\text{Magnetic oxide}\\ \text{of iron.}}}{(\mathrm{FeO, Fe_2O_3})} + \underset{\text{Hydrogen.}}{4\mathrm{H_2}}$$

Action of acids on iron.—Dilute sulphuric acid acts on iron, forming ferrous sulphate and evolving hydrogen.

$$\underset{\text{Iron.}}{\mathrm{Fe}} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{\mathrm{H_2SO_4}} = \underset{\substack{\text{Ferrous}\\ \text{sulphate.}}}{\mathrm{FeSO_4}} + \underset{\text{Hydrogen.}}{\mathrm{H_2}}$$

Strong sulphuric acid, with heat, also acts on iron, but in this case with evolution of sulphur dioxide.

$$\underset{\text{Iron.}}{\mathrm{Fe}} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{2\mathrm{H_2SO_4}} = \underset{\substack{\text{Ferrous}\\ \text{sulphate.}}}{\mathrm{FeSO_4}} + \underset{\substack{\text{Sulphur}\\ \text{dioxide.}}}{\mathrm{SO_2}} + \underset{\text{Water.}}{2\mathrm{H_2O}}$$

Hydrochloric acid acts on iron, forming ferrous chloride, and evolving hydrogen.

$$\underset{\text{Iron}}{\mathrm{Fe}} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{2\mathrm{HCl}} = \underset{\substack{\text{Ferrous}\\ \text{chloride.}}}{\mathrm{FeCl_2}} + \underset{\text{Hydrogen.}}{\mathrm{H_2}}$$

Dilute nitric acid acts on iron, forming ferric nitrate, and evolving nitrogen dioxide. Strong nitric acid does not attack iron.

$$\underset{\text{Iron.}}{\mathrm{Fe}} + \underset{\substack{\text{Nitric}\\ \text{acid.}}}{4\mathrm{HNO_3}} = \underset{\substack{\text{Ferric}\\ \text{nitrate.}}}{\mathrm{Fe(NO_3)_3}} + \underset{\substack{\text{Nitrogen}\\ \text{dioxide.}}}{\mathrm{NO}} + \underset{\text{Water.}}{2\mathrm{H_2O}}$$

Ferrous oxide (FeO) is a black powder obtained by heating ferrous oxalate to 150° in the absence of air.

Ferrous hydrate ($Fe(HO)_2$) is obtained by precipitating a solution of ferrous sulphate with KHO in the absence of air. It is a white substance, very rapidly absorbing oxygen, turning dark green and then gradually rusty brown.

Ferric hydrate ($Fe(HO)_3$) is prepared by precipitating a solution of ferric sulphate or ferric chloride with an alkali, caustic soda being generally employed for the sake of cheapness.

$$\underset{\text{Ferric sulphate.}}{Fe_2(SO_4)_3} + \underset{\text{Sodium hydrate.}}{6NaHO} = \underset{\text{Ferric hydrate.}}{2Fe(HO)_3} + \underset{\text{Sodium sulphate.}}{3Na_2SO_4}$$

Freshly precipitated ferric hydrate is used as an antidote in cases of poisoning by arsenic, the reaction between the ferric hydrate and the arsenic resulting in the formation of the insoluble ferrous arseniate.

$$\underset{\text{Ferric hydrate.}}{4Fe(HO)_3} + \underset{\text{Arsenic.}}{As_2O_3} = \underset{\text{Ferrous arseniate.}}{Fe_3(AsO_4)_2} + \underset{\text{Ferrous hydrate.}}{Fe(HO)_2} + \underset{\text{Water.}}{5H_2O}$$

Freshly precipitated ferric hydrate dissolves in a solution of perchloride of iron, forming a dark red solution of basic chloride of iron; if this solution be placed in a dialyzer, the greater proportion of the hydrochloric acid of this basic chloride passes through the dialyzer, leaving a still more basic chloride of iron.

Freshly precipitated ferric hydrate is also used in the preparation of the iron scale compounds, which are uncrystallisable bodies obtained in the solid form by the evaporation of their solutions to a syrup, and then allowing the syrup to dry in scales. Citrate of iron and ammonium (*Ferri et ammonii citras*) is prepared by dissolving ferric hydrate in a solution of citric acid, adding ammonia, evaporating to a syrup, and drying in scales; it is a double citrate of iron and ammonium. Citrate of iron and quinine (*Ferri et quiniæ citras*) is prepared by dissolving ferric hydrate and quinine in a solution of citric acid, adding ammonia (not in excess, or the quinine would be precipitated), evaporating to a syrup, and drying in scales; it is a triple citrate of iron, quinine, and ammonium. Tartarated iron (*Ferrum tartaratum*) is prepared by dissolving ferric hydrate in a solution of potassium acid tartrate, evaporating to a syrup, and drying in scales; it is a double tartrate of iron and potassium.

Alkaline bicarbonates, which are incompatible with most iron preparations, can be prescribed with citrate of iron and ammonium, and with tartarated iron, without the iron being precipitated; they would not be compatible with citrate of iron and quinine, as the quinine would be thrown down by alkaline carbonates.

Ferric oxide (Fe_2O_3) is prepared by further heating ferric hydrate.

$$\underset{\text{Ferric hydrate.}}{2Fe(HO)_3} = \underset{\text{Ferric oxide.}}{Fe_2O_3} + \underset{\text{Water.}}{3H_2O}$$

It may also be prepared by roasting crystals of ferrous sulphate until fumes of the Nordhausen sulphuric acid cease to be evolved; this variety of ferric oxide passes under the names of *red oxide of iron*, *mineral rouge*, *Venetian red*, *colcothar*, and *crocus*; it is used for polishing.

Ferroso-ferric oxide (FeO,Fe_2O_3) is also known as black oxide of iron and magnetic oxide of iron. It may be prepared (*a*) by passing steam over red-hot iron—

$$\underset{\text{Iron.}}{3Fe} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Ferroso-ferric oxide.}}{Fe_3O_4} + \underset{\text{Hydrogen;}}{4H_2}$$

(*b*) by precipitating a mixed solution of ferric and ferrous sulphates with caustic soda, when the black ferroso-ferric hydrate is thrown down—

$$\underset{\text{Ferric sulphate.}}{Fe_2(SO_4)_3} + \underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Sodium hydrate.}}{8NaHO} =$$

$$\underset{\text{Ferroso-ferric hydrate.}}{Fe(HO)_2, 2Fe(HO)_3} + \underset{\text{Sodium sulphate.}}{4Na_2SO_4}$$

This when heated in a closed vessel loses water and yields the ferroso-ferric oxide.

$$\underset{\text{Ferroso-ferric hydrate.}}{Fe(HO)_2, 2Fe(HO)_3} = \underset{\text{Ferroso-ferric oxide.}}{FeO, Fe_2O_3} + \underset{\text{Water.}}{4H_2O}$$

(*c*) The black *forge-scales*, which collect around the blacksmith's anvil, consist of the ferroso-ferric oxide.

IRON SALTS.

Two classes of iron salts exist, the ferrous and the ferric; in the ferrous salts the iron is only exerting part of its atomicity, and acting as a dyad; whereas in ferric salts it acts as a triad.

FERROUS SALTS.

Ferrous sulphate ($FeSO_4 + 7H_2O$).—This salt is also known as *proto-sulphate of iron, green vitriol, copperas*, and *green copperas*. It is prepared (*a*) by the action of dilute sulphuric acid on iron—

$$\underset{\text{Iron.}}{Fe} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Hydrogen ;}}{H_2}$$

(*b*) by the action of dilute sulphuric acid on ferrous sulphide, this being the ordinary method employed for the preparation of sulphuretted hydrogen—

$$\underset{\text{Ferrous sulphide.}}{FeS} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Sulphuretted hydrogen ;}}{H_2S}$$

(*c*) by gently roasting iron pyrites (FeS_2) in the air.

Ordinary ferrous sulphate contains seven molecules of water of crystallisation ($FeSO_4$, $7H_2O$). By careful heating, six-sevenths of this water can be expelled, leaving the dried sulphate of iron (*Ferri sulphas exsiccatus*) of the composition ($FeSO_4$, H_2O). If further heat be employed, so as to expel this last molecule of water, then the salt is decomposed, ferric oxide being left and Nordhausen sulphuric acid evolved.

If ferrous sulphate be exposed for some time to the air, it loses its green colour and becomes brown, owing to the absorption of oxygen and conversion into basic ferric sulphate.

Ferrous sulphate is very largely employed in the preparation of black writing-ink, the black colour of which is due to tannate of iron in a finely-divided state suspended in weak mucilage, the tannic acid being furnished by an infusion of galls.

Ferrous chloride ($FeCl_2$).—This salt, also known as protochloride of iron, is prepared by the action of hydrochloric acid on iron.

$$\underset{\text{Iron.}}{Fe} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Ferrous chloride.}}{FeCl_2} + \underset{\text{Hydrogen.}}{H_2}$$

Ferrous carbonate ($FeCO_3$) is prepared by mixing together solutions of ferrous sulphate and potassium carbonate, when it is thrown down as a precipitate.

$$\underset{\substack{\text{Ferrous}\\ \text{sulphate.}}}{FeSO_4} + \underset{\substack{\text{Potassium}\\ \text{carbonate.}}}{K_2CO_3} = \underset{\substack{\text{Ferrous}\\ \text{carbonate.}}}{FeCO_3} + \underset{\substack{\text{Potassium}\\ \text{sulphate.}}}{K_2SO_4}$$

Ferrous carbonate is, when first precipitated, of a white colour, but quickly turns green, and ultimately brown from absorption of oxygen from the air, and conversion into ferric oxyhydrate.

The so-called Griffith's mixture (*Mistura ferri composita*) contains green ferrous carbonate in suspension; the absorption of oxygen from the air may be, to a certain extent, prevented by mixing dried ferrous carbonate with sugar (*Ferri carbonas saccharata*). Ferrous carbonate is appreciably soluble in water containing carbon dioxide, and is in this way kept in solution in *chalybeate* spring waters. If such a water be exposed to the air for some time, it becomes turbid from the formation and deposition of ferric hydrate.

Ferrous sulphide (FeS) is prepared by heating a mixture of iron filings and sulphur, or by rubbing a stick of roll sulphur against a bar of iron at a bright red heat; it is a black solid.

Ferrous iodide (FeI_2) is prepared by warming together iron wire, iodine, and water.

Ferrous phosphate ($Fe_3(PO_4)_2$) is prepared by mixing together solutions of ferrous sulphate, sodium phosphate, and sodium bicarbonate.

$$\underset{\substack{\text{Ferrous}\\ \text{sulphate.}}}{3FeSO_4} + \underset{\substack{\text{Sodium}\\ \text{phosphate.}}}{2Na_2HPO_4} + \underset{\substack{\text{Sodium}\\ \text{bicarbonate.}}}{2NaHCO_3} =$$

$$\underset{\substack{\text{Ferrous}\\ \text{phosphate.}}}{Fe_3(PO_4)_2} + \underset{\substack{\text{Sodium}\\ \text{sulphate.}}}{3Na_2SO_4} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{2CO_2} + \underset{\text{Water.}}{2H_2O}$$

The ferrous phosphate comes down at first as a white precipitate, quickly changing to a bluish colour.

The sodium bicarbonate is added to prevent the formation of free sulphuric acid, which would keep some of the ferrous phosphate in solution.

Ferrous arseniate ($Fe_3(AsO_4)_2$) is prepared by mixing together solutions of ferrous sulphate, sodium arseniate, and sodium bicarbonate.

$$\underset{\text{Ferrous sulphate.}}{3FeSO_4} + \underset{\text{Sodium arseniate.}}{2Na_2HAsO_4} + \underset{\text{Sodium bicarbonate.}}{2NaHCO_3} =$$

$$\underset{\text{Ferrous arseniate.}}{Fe_3(AsO_4)_2} + \underset{\text{Sodium sulphate.}}{3Na_2SO_4} + \underset{\text{Carbon dioxide.}}{2CO_2} + \underset{\text{Water.}}{2H_2O}$$

The ferrous arseniate comes down at first as a white precipitate, quickly changing to a greenish colour. The sodium bicarbonate is added for a reason similar to that given in connection with ferrous phosphate.

FERRIC SALTS.

Ferric chloride or **perchloride of iron** ($FeCl_3$).—This may be prepared as black deliquescent plates (*a*) by passing chlorine over heated iron—

$$\underset{\text{Iron.}}{2Fe} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Ferric chloride ;}}{2FeCl_3}$$

(*b*) by passing chlorine through a solution of ferrous chloride (on evaporation it forms a yellow solid)—

$$\underset{\text{Ferrous chloride.}}{2FeCl_2} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Ferric chloride ;}}{2FeCl_3}$$

(*c*) by warming a solution of ferrous chloride with hydrochloric and nitric acids—

$$\underset{\text{Ferrous chloride.}}{3FeCl_2} + \underset{\text{Hydrochloric acid.}}{3HCl} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Ferric chloride.}}{3FeCl_3} + \underset{\text{Nitrogen dioxide.}}{NO} + \underset{\text{Water.}}{2H_2O}$$

This is the process employed in the preparation of the solution of perchloride of iron used in medicine (*Liquor ferri perchloridi*). It really consists in the passage of chlorine into ferrous chloride, since the action of the nitric acid is to oxidise the hydrogen of the hydrochloric acid to water, thus liberating the chlorine, the nitrogen of the nitric acid being evolved as nitrogen dioxide.

Ferric sulphate or **persulphate of iron** ($Fe_2(SO_4)_3$) is prepared by warming together a solution of ferrous sulphate with sulphuric and nitric acids.

$$\underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{6FeSO_4} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3} =$$

$$\underset{\substack{\text{Ferric}\\\text{sulphate.}}}{3Fe_2(SO_4)_3} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

Ferric nitrate or **pernitrate of iron** ($Fe(NO_3)_3 + 6H_2O$) is prepared by the action of dilute nitric acid on iron.

$$\underset{\text{Iron.}}{Fe} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{4HNO_3} = \underset{\substack{\text{Ferric}\\\text{nitrate.}}}{Fe(NO_3)_3} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{NO} + \underset{\text{Water.}}{2H_2O}$$

Ferric acetate or **peracetate of iron** ($Fe(C_2H_3O_2)_3$) is prepared by dissolving freshly precipitated ferric hydrate in glacial acetic acid.

Iron and cyanogen compounds. (*See* Organic Chemistry, Chapter III.).

General methods of raising ferrous salts to the ferric state.—(*a*) The passage of chlorine gas through a solution of a ferrous salt raises it to the ferric state, thus :

$$\underset{\substack{\text{Ferrous}\\\text{chloride}}}{2FeCl_2} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Ferric}\\\text{chloride.}}}{2FeCl_3}$$

$$\underset{\text{Ferrous sulphate.}}{6FeSO_4} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Ferric sulphate.}}{2Fe_2(SO_4)_3} + \underset{\text{Ferric chloride.}}{2FeCl_3}$$

(*b*) Nitric acid with heat will raise any ferrous salt to the ferric state, thus:

$$\underset{\text{Ferrous chloride.}}{3FeCl_2} + \underset{\text{Nitric acid.}}{4HNO_3} = \underset{\text{Ferric chloride.}}{2FeCl_3} + \underset{\text{Ferric nitrate.}}{Fe(NO_3)_3} + \underset{\text{Nitrogen dioxide.}}{NO} + \underset{\text{Water.}}{2H_2O}$$

$$\underset{\text{Ferrous sulphate.}}{3FeSO_4} + \underset{\text{Nitric acid.}}{4HNO_3} = \underset{\text{Ferric sulphate.}}{Fe_2(SO_4)_3} + \underset{\text{Ferric nitrate.}}{Fe(NO_3)_3} + \underset{\text{Nitrogen dioxide.}}{NO} + \underset{\text{Water.}}{2H_2O}$$

(*c*) Long-continued exposure to air will convert most, and heating in the air will convert all ferrous salts into ferric salts.

General methods of reducing ferric salts to the ferrous state.—(*a*) If to a solution of a ferric salt some zinc be added, and then sufficient hydrochloric acid to act on the zinc and liberate hydrogen, the nascent hydrogen will reduce the ferric salt to the ferrous state.

$$\underset{\text{Ferric chloride.}}{2FeCl_3} + \underset{\text{Hydrogen}}{H_2} = \underset{\text{Ferrous chloride.}}{2FeCl_2} + \underset{\text{Hydrochloric acid.}}{2HCl}$$

(*b*) If sulphuretted hydrogen be passed through a solution of a ferric salt, the latter will be reduced to the ferrous state, sulphur being thrown down.

$$\underset{\text{Ferric chloride.}}{4FeCl_3} + \underset{\text{Sulphuretted hydrogen.}}{2H_2S} = \underset{\text{Ferrous chloride.}}{4FeCl_2} + \underset{\text{Hydrochloric acid.}}{4HCl} + \underset{\text{Sulphur.}}{S_2}$$

(*c*) If to a solution of a ferric salt, solution of stannous chloride be added, the former will be reduced to the ferrous state, the latter being raised to the stannic state.

$$\underset{\substack{\text{Ferric}\\ \text{chloride.}}}{2FeCl_3} + \underset{\substack{\text{Stannous}\\ \text{chloride.}}}{SnCl_2} = \underset{\substack{\text{Ferrous}\\ \text{chloride.}}}{2FeCl_2} + \underset{\substack{\text{Stannic}\\ \text{chloride.}}}{SnCl_4}$$

Tests for iron occurring as a ferrous salt.

(i) Ammonium sulphide gives a black precipitate of ferrous sulphide.

(ii) Sulphuretted hydrogen gives no precipitate with a ferrous salt in acid solutions. This negative reaction is of value in the separation from iron of metals precipitated by sulphuretted hydrogen.

(iii) Potassium ferrocyanide (K_4FeCy_6) gives with ferrous salts a precipitate, at first almost white, but rapidly changing to a light blue colour, owing to absorption of oxygen from the air. This precipitate is a double ferrocyanide of iron in the ferrous state and potassium (FeK_2FeCy_6).

(iv) Potassium ferricyanide (K_3FeCy_6) gives with ferrous salts a dark blue precipitate (KFe_2Cy_6), sometimes, though erroneously, called Turnbull's blue ($Fe_3Fe_2Cy_{12}$).

(v) Potassium sulphocyanide gives no colour with ferrous salts, provided they are quite free from ferric salts.

(vi) Alkalies, such as ammonia, potash, and soda, partially precipitate ferrous salts as ferrous hydrate, the precipitate being white at first, but rapidly turning to a greenish colour from absorption of oxygen from the air, and then slowly becoming rusty brown.

Tests for iron occurring as a ferric salt.

(i) Ammonium sulphide reduces a ferric salt to the ferrous state, producing a mixed precipitate of the black ferrous sulphide and sulphur.

(ii) Sulphuretted hydrogen passed through a solution of a ferric salt reduces it to the ferrous state, sulphur being precipitated.

(iii) Potassium ferrocyanide (K_4FeCy_6) gives a dark blue precipitate (KFe_2Cy_6), sometimes, though erroneously, called Prussian blue ($Fe_4(FeCy_6)_3$).

(iv) Potassium ferricyanide gives with a solution of a ferric salt a brownish colour, no precipitate being produced.

Olive Green

(v) Potassium sulphocyanide gives with solutions of ferric salts a deep blood-red colour, due to the formation of the soluble ferric sulphocyanide.

(vi) The alkalies, ammonia, potash, and soda, precipitate from ferric solutions the reddish-brown ferric hydrate.

DISTINGUISHING TESTS BETWEEN FERROUS AND FERRIC SALTS.

	FERROUS SALTS.	FERRIC SALTS.
Potassium ferrocyanide.	Light blue precip.	Dark blue precip.
Potassium ferricyanide.	Dark blue precip.	No precip.; brownish colour produced.
Potassium sulphocyanide.	No change of colour *if the ferrous salt is pure.*	Dark blood-red colour.
Alkalies . . .	Green precip., turning rusty brown on surface.	Reddish-brown precipitate.

Cobalt and nickel.—These metals occur in nature usually in combination with arsenic and sulphur, from which the metals are extracted by a somewhat complex process. Both metals are hard, magnetic, malleable, and white, nickel having a yellowish tinge. They melt at very high temperatures, and are both used for plating iron, brass, etc.

The *cobalt salts*, when hydrated, are usually pink in colour, but when rendered anhydrous by heat they become blue.

The most common salt is the nitrate ($CO(NO_3)_2 + 6H_2O$); it is used as a test, in the dry way, for aluminium, zinc, and magnesium compounds.

Nickel has become recently of great importance in connection with the steel industry, since steel, by the addition of about 5 per cent. of nickel, has its tensile strength increased about one-half. Very valuable deposits of nickel sulphide were found in Canada during the construction of the Canadian Pacific Railway. Much nickel is used for making German silver, which is brass (copper and zinc), alloyed with 10 to 20 per cent. of nickel. The nickel salts are usually green.

Cobalt compounds give a blue colour to a borax bead and to glass, nickel compounds give a smoke-coloured borax bead.

Nickel forms a colourless volatile liquid with carbon monoxide. No such compound with cobalt is known.

CHAPTER VIII.

COPPER—SILVER—GOLD—PLATINUM.

Copper—Natural Compounds of Copper—Preparation and Properties of Metallic Copper—Action of Acids on Copper—Copper Salts—Tests for Copper—Silver—Extraction and Properties of Metallic Silver—Silver Salts—Tests for Silver, Gold, Platinum.

COPPER.

Symbol, Cu; *dyad; atomic weight*, 63·6; *specific gravity*, 8·9; *melts*, 1080°.

Natural compounds of copper.—(i) The commonest copper ore is *copper pyrites*, a double sulphide of copper and iron ($CuFeS_2$), containing in addition some sulphide of arsenic. (ii) *Cuprite* or *red copper ore* consists of cuprous oxide (Cu_2O). (iii) *Malachite* is a double carbonate and hydrate of copper ($CuCO_3$, $Cu(HO)_2$). (iv) The metal copper is found to a certain extent free in nature, occurring especially in North America.

Preparation of the metal copper.—The separation of metallic copper from copper pyrites is a lengthy and complicated process; briefly described, the copper ore is first roasted, the temperature is then raised till the ore fuses; the two chief products are cuprous sulphide and silicate of iron: the silicate of iron is separated; by repeating the roasting and fusing all the iron is removed as silicate. The nearly pure cuprous sulphide is then carefully roasted until two-thirds are converted into oxide. The temperature is then raised, and the following reaction takes place:

$$\underset{\text{Cuprous oxide.}}{2Cu_2O} + \underset{\text{Cuprous sulphide.}}{Cu_2S} = \underset{\text{Copper.}}{6Cu} + \underset{\text{Sulphur dioxide.}}{SO_2}$$

The copper is remelted and stirred up with a pole of wood to reduce any oxide which may be present.

Chemically pure copper may be obtained by passing hydrogen over copper oxide raised to a red heat or by electrolysis.

$$\underset{\text{Copper oxide.}}{2CuO} + \underset{\text{Hydrogen.}}{2H_2} = \underset{\text{Copper.}}{2Cu} + \underset{\text{Water.}}{2H_2O}$$

Properties of the metal copper.—Copper is one of the few metals possessing a distinctive colour—it is bright red; it is a very malleable and ductile metal, and is an extremely good conductor of both heat and electricity, hence its employment for lightning conductors, etc. Copper remains unchanged in dry air, but in moist air it becomes gradually covered with a green layer of a basic copper carbonate, frequently mistaken for verdigris (oxyacetate of copper). Water can be boiled in copper vessels without attacking them, but a solution of common salt slowly attacks copper, forming a green oxychloride of copper, and vinegar still more readily acts on copper vessels forming verdigris (oxyacetate of copper); hence the danger of using copper vessels for culinary purposes, the copper salts produced by the action of common salt and vinegar being poisonous. Copper does not decompose steam, even at a bright red heat; if copper be heated to redness in the air, it readily oxidises, forming the black copper oxide (CuO). The metal copper is deposited from its solutions by either iron or zinc, and it is also deposited at the negative pole when an electric current is passed through a solution of copper sulphate, a process employed in producing electrotypes or copies of objects in copper.

Copper enters into the formation of several very useful alloys. *Brass* contains about 70 parts of copper to 30 parts of zinc; a larger proportion of zinc yields an alloy of a pale yellow colour, known as *Muntz metal*, largely used for covering wooden ships; by increasing the amount of copper, and adding a little tin, *Dutch metal* is obtained. *Bronze*, *gun-metal*, and *bell-metal* are alloys of copper and tin containing from 80 to 90 per cent. of copper; *speculum metal* is a hard white alloy of 2 parts of copper to 1 part of tin with a little arsenic; it is capable of taking a high polish, and is used for the mirrors of reflecting telescopes. *German silver* or *nickel silver* is an alloy of copper, zinc, and nickel; all silver articles and silver coins contain some copper, in order to render the silver harder; *aluminium bronze* or *aluminium gold* is an alloy of copper and aluminium.

Action of acids on copper.—Dilute sulphuric acid has no action on the metal copper. Strong sulphuric acid with heat readily acts on copper, forming the sulphate and evolving sulphur dioxide gas.

$$\underset{\text{Copper.}}{\mathrm{Cu}} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{2\mathrm{H_2SO_4}} = \underset{\substack{\text{Copper}\\ \text{sulphate.}}}{\mathrm{CuSO_4}} + \underset{\substack{\text{Sulphur}\\ \text{dioxide.}}}{\mathrm{SO_2}} + \underset{\text{Water.}}{2\mathrm{H_2O}}$$

Nitric acid readily acts on copper, forming copper nitrate, with evolution of nitrogen dioxide.

$$\underset{\text{Copper.}}{3\mathrm{Cu}} + \underset{\substack{\text{Nitric}\\ \text{acid.}}}{8\mathrm{HNO_3}} = \underset{\substack{\text{Copper}\\ \text{nitrate.}}}{3\mathrm{Cu(NO_3)_2}} + \underset{\substack{\text{Nitrogen}\\ \text{dioxide.}}}{2\mathrm{NO}} + \underset{\text{Water.}}{4\mathrm{H_2O}}$$

Hydrochloric acid has no action on copper.

Cuprous oxide (Cu_2O).—Red oxide of copper is best prepared by boiling a mixed solution of copper sulphate, grape sugar, and caustic potash or soda; in the absence of the grape sugar, cupric oxide (CuO) would be thrown down, but the grape sugar possesses the property of abstracting one-half of the oxygen from the cupric oxide, with the consequent formation and precipitation of the red cuprous oxide. This constitutes the test for sugar in diabetic urine.

Cupric oxide (CuO).—Black copper oxide may be obtained (*a*) by roasting metallic copper in air, (*b*) by heating copper nitrate—

$$\underset{\text{Copper nitrate.}}{2Cu(NO_3)_2} = \underset{\text{Cupric oxide.}}{2CuO} + \underset{\text{Nitrogen tetroxide.}}{4NO_2} + \underset{\text{Oxygen ;}}{O_2}$$

(*c*) by adding caustic soda to a solution of copper sulphate to precipitate the light blue copper hydrate ($Cu(HO)_2$), and then boiling the liquid, when the copper hydrate decomposes into cupric oxide and water.

$$\underset{\text{Copper hydrate.}}{Cu(HO)_2} = \underset{\text{Cupric oxide.}}{CuO} + \underset{\text{Water.}}{H_2O}$$

COPPER SALTS.

Copper forms two classes of compounds, *cupric* and *cuprous*; in both classes the copper is acting as a dyad, but all cuprous compounds contain in the molecule two atoms of copper, and as these two atoms are linked together by an atom-fixing power of each, the copper atoms only exert towards other elements the atom-fixing power of a monad; this will be rendered evident by inspection of the following graphic formulæ of cupric chloride ($CuCl_2$) and cuprous chloride (Cu_2Cl_2).

$$\underset{\text{Cupric chloride.}}{Cl - Cu - Cl} \qquad \underset{\text{Cuprous chloride.}}{Cl - Cu - Cu - Cl}$$

Copper sulphate ($CuSO_4 + 5H_2O$).—This, the commonest salt of copper, is also known as *blue vitriol* and *bluestone*. It is prepared (*a*) by the action of hot strong sulphuric acid on the metal copper—

$$\underset{\text{Copper.}}{Cu} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Copper}\\\text{sulphate.}}}{CuSO_4} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{SO_2} + \underset{\text{Water ;}}{2H_2O}$$

the result of the action is a greyish powder, consisting of anhydrous copper sulphate with some sulphide; on pouring off the strong sulphuric acid and adding water, a blue solution is obtained which is filtered and evaporated, when crystals of ordinary copper sulphate or *blue vitriol* separate;

(*b*) by the action of dilute sulphuric acid on cupric oxide—

$$\underset{\substack{\text{Cupric}\\\text{oxide.}}}{CuO} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Copper}\\\text{sulphate.}}}{CuSO_4} + \underset{\text{Water ;}}{H_2O}$$

(*c*) by roasting copper pyrites in the air, by which process it is obtained mixed with sulphate of iron.

Copper sulphate in its crystalline condition contains five molecules of water of crystallisation ($CuSO_4$, $5H_2O$); these can be expelled by heat, leaving the anhydrous copper sulphate ($CuSO_4$), which is of a se of CuSO to detect water [illegible]

white colour; if this anhydrous copper sulphate is shaken with liquids containing water, it unites with the water forming the blue crystalline variety, and hence becomes a valuable test for the detection of water in liquids which should, if pure, be free from it, such as absolute alcohol.

Copper nitrate ($Cu(NO_3)_2 + 3H_2O$) is prepared by the action of nitric acid on copper.

$$\underset{\text{Copper.}}{3Cu} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Copper nitrate.}}{3Cu(NO_3)_2} + \underset{\text{Nitrogen dioxide.}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

Copper oxyacetate (verdigris) ($Cu(C_2H_3O_2)_2$, $2CuO + 3H_2O$) is prepared by exposing copper to the vapour of acetic acid and the action of the air.

Copper arsenite (Scheele's green) ($CuHAsO_3$) is prepared by mixing solutions of copper sulphate and sodium arsenite, when it is thrown down as a bright green precipitate.

$$\underset{\text{Copper sulphate.}}{CuSO_4} + \underset{\text{Sodium arsenite.}}{Na_2HAsO_3} = \underset{\text{Scheele's green.}}{CuHAsO_3} + \underset{\text{Sodium sulphate.}}{Na_2SO_4}$$

Scheele's green is very poisonous, mainly on account of the arsenic contained in it; it is a pigment frequently employed in the colouring of wall-papers, book-covers, etc. For the methods of detecting it in wall-papers, etc., *see* pages 287, 289.

Tests for Copper.

(i) Sulphuretted hydrogen passed into copper solutions gives a black precipitate of copper sulphide (CuS).

Na

K

(ii) Ammonium sulphide gives a similar precipitate of the black copper sulphide.

(iii) Potassium ferrocyanide with acetic acid give a reddish-brown precipitate of copper ferrocyanide (Cu_2FeCy_6). This is the most delicate test for copper, as an extremely dilute solution of a copper salt is tinted reddish-brown on the addition of potassium ferrocyanide.

(iv) Solution of ammonia gives a light blue precipitate of copper hydrate ($Cu(HO)_2$), readily soluble in excess of ammonia and yielding an intensely dark blue solution. This is a very delicate test for copper salts.

(v) Solution of caustic potash or caustic soda produces a light blue precipitate of copper hydrate, not soluble in excess of the fixed alkali; on boiling the liquid, the light blue precipitate turns black, owing to the decomposition of the copper hydrate into cupric oxide and water.

(vi) A piece of bright steel, such as the polished steel blade of a knife, if immersed in an acid solution of a copper salt, becomes in a short time coloured with a reddish deposit of the metal copper upon it. This is a ready and useful test for ascertaining whether a blue liquid contains copper or not.

(vii) Copper salts give a green colour to the Bunsen flame, except the chloride, which gives a blue colour.

(viii) When fused into borax copper salts give in the outer flame a bead which is green when hot and blue when cold; in the inner flame the bead becomes red and opaque.

HNO_3 } black pp Sol.

blackening with heat

reddish brown

Bright steel coppered.

Lead
Copper
Antimony

SILVER.

Symbol, Ag; *monad; atomic weight*, 108; *specific gravity*, 10·56; *melts at* 960°.

Occurrence in nature.—Silver occurs free in nature; also as *horn silver* (AgCl); *sulphide of silver* (Ag_2S) is frequently contained in other native sulphides, notably in those of lead, copper, and antimony.

Extraction of the metal silver.—The *cupellation process* for extracting silver from lead has already been described in connection with the latter metal (*see* page 271). The *amalgamation process* for the extraction of silver consists in roasting the silver ores with common salt (sodium chloride), by which means silver chloride is formed; the roasted ores are then agitated in barrels with water and scrap iron, the iron abstracting the chlorine from the silver chloride to form ferrous chloride, and setting free the metal silver; mercury is then introduced into the barrels and they are again thoroughly agitated, when an amalgam of mercury and silver is formed; this amalgam is removed and heated in retorts, when the mercury distils over, the metal silver being left in the retort. In Mexico the silver ore is ground with water, salt and copper sulphate, and thereby converted into chloride of silver. Mercury is now added and an amalgam of silver formed which is heated as above.

Roast with NaCl

$$\underset{\text{Silver chloride.}}{2AgCl} + \underset{\text{Mercury.}}{2Hg} = \underset{\text{Calomel.}}{Hg_2Cl_2} + \underset{\text{Silver.}}{2Ag}$$

Properties of the metal silver.—Silver is a white, lustrous metal; it is soft, and so malleable that it can be beaten into extremely thin leaves (*silver leaf*). It does not oxidise at any temperature in the air, but in the molten state it possesses the peculiar power of dissolving about 20 times its volume of oxygen from the air; this oxygen is given off when the silver cools and solidifies, producing the phenomenon known as the *spitting* of silver. Sulphuretted hydrogen blackens silver, and hence polished silver articles slowly tarnish when exposed to the air. Pure silver is too soft for use, but by the admixture of a small amount of copper with it, a hard alloy is obtained. Standard silver contains 92·5 per cent. of silver and 7·5 per cent. of copper. To prepare a specimen of pure silver from a coin, dissolve in nitric acid, to the green solution add hydrochloric acid, when the silver is precipitated as silver chloride; this is washed till free from copper and then fused with sodium carbonate.

$$\underset{\text{Silver chloride.}}{2AgCl} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} = \underset{\text{Salt.}}{2NaCl} + \underset{\text{Silver.}}{2Ag} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Oxygen.}}{O}$$

Action of acids on silver.—Hydrochloric acid does not attack silver. Nitric acid forms silver nitrate, with evolution of nitrogen dioxide.

$$\underset{\text{Silver.}}{3Ag} + \underset{\text{Nitric acid.}}{4HNO_3} = \underset{\text{Silver nitrate.}}{3AgNO_3} + \underset{\text{Nitrogen dioxide.}}{NO} + \underset{\text{Water.}}{2H_2O}$$

Hot strong sulphuric acid acts on silver, forming silver sulphate and evolving sulphur dioxide.

$$\underset{\text{Silver.}}{2Ag} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Silver sulphate.}}{Ag_2SO_4} + \underset{\text{Sulphur dioxide.}}{SO_2} + \underset{\text{Water.}}{2H_2O}$$

Silver oxide (Ag_2O) is prepared by precipitating a solution of silver nitrate with a solution of potash, soda, or lime; lime-water is preferable on account of its freedom from chlorides.

K
Na
Ca(

$$\underset{\text{Silver nitrate.}}{2AgNO_3} + \underset{\text{Calcium hydrate.}}{Ca(HO)_2} = \underset{\text{Silver oxide.}}{Ag_2O}$$

$$+ \underset{\text{Calcium nitrate.}}{Ca(NO_3)_2} + \underset{\text{Water.}}{H_2O}$$

Silver oxide is a brown powder, which is reduced to the metallic state either by heat or by contact with organic matter; on account of this last-mentioned property it should not be used in medicine combined with an essential oil or other organic substance.

SILVER SALTS.

Silver nitrate ($AgNO_3$) is prepared by the action of nitric acid on silver (*see* above). If silver nitrate is carefully melted, and then poured into moulds, it solidifies in the form of sticks, known as *lunar caustic*, a substance frequently employed for external application as a caustic. The blackening produced on the skin after the application of silver nitrate is due to the reduction of the salt to metallic silver. A weaker caustic known as *mitigated caustic* is a mixture of silver and potassium nitrates, and is prepared by fusing together one part of silver nitrate with two parts of potassium nitrate.

Silver chloride, bromide and **iodide.**—These compounds are obtained as precipitates when the corresponding potassium salts are added to a solution of silver nitrate. They are all very sensitive to the action of light, becoming reduced to a sub-salt after exposure, and this sub-salt, if afterwards treated with a reducing agent, becomes converted into metallic silver. It is on account of their sensitiveness to light that these silver salts are used in the production of photographs. The dry plates now used in photography consist of glass plates covered with a film of silver iodide or bromide suspended in gelatine; these plates are exposed in the camera to the light reflected from the object to be photographed; where the light falls, the silver salt is more or less reduced to a sub-salt, according to the intensity of the light. If the exposed plate is now placed in a solution of a reducing agent, such as pyrogallic acid and ammonia, the sub-salt is completely reduced to metallic silver; this is the process known as *developing.* To preserve this picture and to prevent the undecomposed silver salt from blackening when exposed to the light, it must now be *fixed;* this process consists in dissolving out the undecomposed bromide or iodide of silver by immersing the plate in a solution of sodium thiosulphate (hyposulphite of soda). (*See* page 204.)

The Process of Development

In this way a *negative* is obtained, showing the bright parts of the object dark and the dark parts light; to *print* an ordinary photograph on to paper, the negative is placed over a sheet of paper prepared with silver chloride, and then exposed to the light.

Silver chloride is white, but rapidly darkens when exposed to daylight. When heated it melts, and, on cooling, forms a dark brown mass like horn, hence it is sometimes called *horn silver.* Silver bromide is whitish in colour, silver iodide is pale yellow and is insoluble in ammonia.

HCl gives white pp.

Tests for Silver.

Graph I

(i) Hydrochloric acid gives, with solutions of silver salts, a white curdy precipitate of silver chloride,

HCl | Am H | K_2CrO_4

insol in hot water,

insoluble in nitric acid, but soluble in solution of ammonia.

(ii) Potassium chromate gives, with a neutral solution of a silver salt, a red precipitate of silver chromate. Sol in hot HNO_3.

(iii) Sodium phosphate gives, with a neutral solution of a silver salt, a yellow precipitate of silver phosphate.

iv KI. gives pale yellow pp. insol in dil HNO_3 & in NH_4OH.

v. Zn + H_2SO_4 (dil) gives grey metallic Ag.

GOLD.

Symbol, Au; *triad; atomic weight*, 197·2; *specific gravity*, 19·4; *melts at* 1250°.

Gold occurs in nature in the free state. It is found in masses called nuggets, and also, in a more finely-divided state, in quartz rocks and in alluvial quartz sand which has been deposited by the disintegration of the older rocks. It is extracted by shaking with mercury, or by dissolving it out (1) by chlorine water, or (2) by a weak solution of sodium cyanide. Pure gold is prepared by melting ordinary gold with three parts of silver, and then dissolving out the silver either with nitric acid or by boiling strong sulphuric acid, when the gold is left as a brown powder.

Gold is one of the few metals possessing a decided tint, and is distinguished by its yellow colour. It is soft and very malleable, and can be beaten out into thin leaves (*gold-leaf*). It can be hammered so thin as to transmit light, the light being of a bluish-green colour. Gold is too soft a metal for general use, and is therefore alloyed with copper, in order to produce a hard alloy, which does not so readily wear away when used. The fineness of a sample of gold is in England expressed in *carats*, pure gold being said to be 24 carats. Thus, 18-carat gold consists of 18 parts of gold alloyed with 6 parts of copper; 15-carat gold consists of 15 parts of gold alloyed with 9 parts of copper, and so on. English sovereigns and half-sovereigns are made of 22-carat gold, that is, of 22 parts of gold alloyed with 2 parts of copper.

Gold is not attacked by sulphuric, hydrochloric, or nitric acids separately; it is acted on by aqua regia (nitro-hydrochloric acid), auric chloride ($AuCl_3$) being formed, and nitrogen dioxide evolved.

$$\underset{\text{Gold.}}{Au} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{3HCl} + \underset{\substack{\text{Nitric}\\ \text{acid.}}}{HNO_3} = \underset{\substack{\text{Auric}\\ \text{chloride.}}}{AuCl_3} + \underset{\substack{\text{Nitrogen}\\ \text{dioxide.}}}{NO} + \underset{\text{Water.}}{2H_2O}$$

PLATINUM.

Symbol, Pt; *tetrad; atomic weight*, 195; *specific gravity*, 21·7; *melts at* 2000°.

Platinum occurs in nature in the metallic state mixed with quartz. It is a very tough metal, and on account of the very high temperature (2000° C.) required to melt it, it is very suitable for the manufacture of crucibles, dishes, etc., used for analytical work. Platinum may be obtained as a grey spongy mass, called *spongy platinum*, by heating the double chloride of platinum and ammonium ($PtCl_4$, $2NH_4Cl$); this spongy platinum is very porous, and possesses the power of occluding, or condensing within its pores, oxygen from the atmosphere. This occluded oxygen is so active that, if a stream of hydrogen is directed on to spongy platinum, the platinum first becomes red-hot, and then ignites the hydrogen. Döbereiner's hydrogen lamp depends upon this property of spongy platinum igniting a jet of hydrogen.

Platinum is not attacked by sulphuric, hydrochloric, or nitric acids separately; it is acted on by aqua regia (nitro-hydrochloric acid), platinic chloride ($PtCl_4$) being formed, and nitrogen dioxide evolved.

Three of the metals discussed in this chapter, viz. copper, silver and gold, find their place, in the periodic classification (page 208), in the first column, following under the metal sodium; their points of resemblance with that metal are not numerous, whereas their points of difference are striking. Thus, they do not decompose water at ordinary temperatures; they occur in nature in the metallic state. Silver is a monovalent metal, and resembles sodium in the fact that it forms an alum with aluminium sulphate; on the other hand, copper is divalent and gold trivalent in their most characteristic compounds. Platinum comes in the eighth column, among the difficultly fusible metals. By some chemists the metals mercury, silver, gold, and platinum have been classed together as the *noble* metals because their oxides are reduced to the metallic state by the action of heat alone.

Part IV.

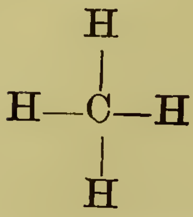
ORGANIC CHEMISTRY.

CHAPTER I.

ORGANIC COMPOUNDS.

Organic Compounds—Organic Radicles—Destructive or Dry Distillation—Decay—Fermentation—Putrefaction.

ORGANIC chemistry includes the chemistry of the organic compounds. The term *organic* is derived from ὄργανον, *an organ.* Originally organic chemistry only included the chemistry of those compounds formed in plants and animals as the result of the vital processes occurring in their cells and tissues; at that time it was believed that organic compounds could not be prepared artificially, but were only formed as the result of the vital processes taking place in plants and animals. This distinction is now well known to be erroneous, a number of organic substances having been artificially prepared, either from their elements or from inorganic compounds. For instance, *cyanogen* (C_2N_2), *acetylene* (C_2H_2), *urea* ($CO(NH_2)_2$), alcohol (C_2H_5HO), and many other organic substances have been artificially prepared from purely inorganic materials. All organic bodies contain the element carbon; this element is a tetrad, and has four points, to which other elements can attach themselves, as we see in Marsh gas (CH_4).

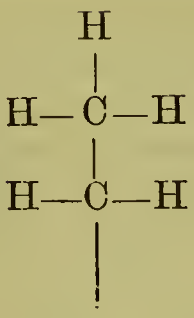


$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

Marsh Gas.

Carbon has, moreover, a power of linking itself atom to atom, to form with other elements stable compounds of great complexity, which is quite unique; thus, the red colouring matter of the blood, hæmoglobin, is believed to contain in its molecule 600 atoms of carbon, 960 of hydrogen, 154 of nitrogen, 179 of oxygen, besides 3 atoms of sulphur and 1 of iron. No other element seems capable of forming compounds of such complexity. As carbon plays such an important part, organic chemistry may be shortly defined as *the chemistry of the carbon compounds*, excluding the two oxides and sulphides of carbon (CO, CO_2, CS_2, CS), which are usually classed as inorganic substances.

We may look at organic chemistry from another point of view, which is very instructive. In the inorganic part the number of elements is large, but the number of compounds of any one element (excluding carbon) is comparatively small. In the organic compounds the number of elements is small, but the number of the compounds of these few elements seems almost unlimited. The elements, in fact, of the inorganic portion are represented in organic bodies by the groups of elements called *radicles*; for instance, taking the element potassium, we have its hydrate, its oxide, its chloride, its sulphate, etc.; parallel series of compounds are formed by many organic radicles. We will take as an example ethyl (C_2H_5); this is a monovalent radicle, as can be seen from its graphic formula:



Ethyl Alcohol.

This radicle forms a hydrate or hydroxide (ordinary alcohol), an oxide (ordinary ether), etc. Thus, we have a parallel series of bodies, as can be seen from the following table :—

K'	$(C_2H_5)'$	
KHO	$(C_2H_5)HO$	alcohol
K_2O	$(C_2H_5)_2O$	ether
~~KCl~~	~~$(C_2H_5)Cl$~~	
K_2SO_4	$(C_2H_5)_2SO_4$	

Now, there is an enormous number of these radicles, each forming its own compounds, just as each metal has its own oxides, salts, etc.

It has already been seen how the various elements fall into two main groups—the non-metals (as Cl, Br, etc.), or electro-negative elements, and the metals (as K, Ca, etc.), or electro-positive elements. In the same way we have electro-negative radicles, as cyanogen (CN), the radicles of the organic acids, acetyl (C_2H_3O), etc., and electro-positive radicles, methyl (CH_3), ethyl (C_2H_5), phenyl (C_6H_5), etc.

These radicles in organic chemistry take the place of the elements in inorganic bodies, and so, from this point of view, we may define organic chemistry as *the chemistry of the compound radicles.*

It is very important not to confuse an *organic body* or *compound* with an *organised body.* The definition of an organic body or compound has just been given; an organised body is a tissue of fibrous or cellular nature, the result of animal or vegetable growth, and which cannot be made artificially.

Elements composing organic compounds.—Although the number of organic compounds far exceeds that of the inorganic bodies, yet the actual number of elements entering into the composition of the great majority of organic substances is small. One large group, the *hydrocarbons*, contains only two elements, carbon and hydrogen; another great class contains oxygen in addition, this includes the *carbohydrates* (starch, sugar, etc.) and most of the organic acids; in fact, a very large proportion of organic bodies contain not more than four elements (carbon, hydrogen, oxygen, and nitrogen); chlorine, bromine, iodine, sulphur, and phosphorus enter into the composition of a few, whilst metallic elements are contained in a small number of organic bodies. The fact, however, should be borne in mind that any element can be made to enter into the composition of an artificially prepared organic compound.

Action of heat on organic bodies.—With the exception of those organic substances that volatilise unchanged when heated, most organic bodies are distinguished by the facility with which they are decomposed on the application of heat. If heated to a sufficiently high temperature with free contact of air, they burn away, the carbon forming carbon dioxide, the hydrogen forming water, and the nitrogen escaping in the free state or as ammonia. If heated out of contact with the air, most organic bodies undergo a complex decomposition, known as *destructive* or *dry distillation*, a number of fresh bodies being produced by a rearrangement of the atoms of the organic molecule under the influence of dry heat, without contact of air. For examples of destructive or dry distillation, *see* pages 392, 432.

Decay.—Many moist organic substances when exposed to the air undergo a slow process of oxidation and so are gradually destroyed without sensible elevation of temperature; this slow combustion or oxidation is called *decay*.

Fermentation.—This name is applied to a class of decompositions that many organic bodies undergo in presence of a ferment. There are two classes of ferments, the *organised* and the *non-organised.* The *organised ferments* are microscopic organisms, as *yeast* or *torula cerevisiæ*, which produces alcoholic or vinous fermentation, *mycoderma aceti*, which produces acetous fermentation, and *penicillium glaucum*, which produces lactic and probably butyric fermentation.

The various micro-organisms (bacilli, etc.) that have been discovered in connection with several of the zymotic diseases, and which are apparently the primary causative factors of the diseases, possibly act as ferments within the human body, producing organic poisons, the presence of which in the system may be the direct cause of the symptoms of the various diseases. The *non-organised* or *soluble ferments* act only in solution, and when isolated are obtained as amorphous powders, as, for example, *pepsin*, the ferment contained in gastric juice, *ptyalin*, the ferment contained in saliva, and *trypsin*, the ferment contained in pancreatic juice.

In the case of the organised ferments, the fermentative process is probably due to the ferment growing and multiplying at the expense of part of the substance that is being acted on, the remaining part breaking up into simpler bodies, which are the products of fermentation; in other words, the ferment is regarded as feeding, for its growth and multiplication, on a small portion of the substance undergoing fermentation, and thus destroying the chemical balance of the remaining portion, so as to cause its resolution into simpler bodies.

Putrefaction.—This process is practically one of fermentation produced in nitrogenised organic bodies by bacteria and other ferments, and accompanied by the evolution of unpleasant-smelling gases, which are mainly compounds of sulphur and phosphorus, and in part, possibly, complex hydrocarbon gases and volatile nitrogenous bases. The conditions necessary for putrefaction are (*a*) the presence of a certain amount of air to start the process, (*b*) moisture, and (*c*) warmth. If air is excluded, as in the proper tinning of tinned provisions, and if bacteria and other ferments are previously destroyed by heat, then putrefaction does not occur. Disinfectants prevent putrefaction by their germicidal action; that is, by destroying the ferments that set up the putrefactive changes.

CHAPTER II.

ULTIMATE ANALYSIS OF ORGANIC COMPOUNDS.

Determination of Carbon, Hydrogen, Oxygen, Nitrogen, Chlorine, Sulphur, and Phosphorus in Organic Bodies—Calculation of Formulæ from Percentage Composition—Empirical, Molecular, and Constitutional Formulæ—Determination of Molecular Weight—Isomeric Bodies.

SINCE so large a number of organic compounds only contain carbon, hydrogen, and oxygen, their ultimate analysis consists in determining the amount of carbon in the form of carbon dioxide, the amount of hydrogen in the form of water, the amount of oxygen being always determined by difference. The determinations of the amounts of other elements, such as nitrogen, chlorine, bromine, iodine, sulphur, and phosphorus, are always made separately.

Determination of the carbon and hydrogen in an organic compound containing carbon, hydrogen, and oxygen.—A weighed quantity of the dried organic compound (sugar, for instance) is taken, and its carbon is converted into carbon dioxide, and its hydrogen into water, by burning it in a stream of oxygen in a tube containing copper oxide; the water is collected in a previously-weighed calcium chloride tube (Fig. 29), and the carbon dioxide in a strong solution of caustic potash contained in a series of bulbs (Fig. 30), which are weighed with the caustic potash previous to the operation.

The combustion is carried out in a thick combustion-tube, about 24 inches long, made of hard glass (Fig. 31), the fore part of which is charged with well-dried granular copper oxide (C), a plug of asbestos (D) being placed in front of it to prevent the mechanical carrying over of any of the copper oxide. The weighed quantity of sugar is placed in a small platinum boat (B), which is then slipped into the tube as shown in the figure, and the tube is placed in a gas combustion-furnace, with the ends projecting from either extremity of the furnace; the

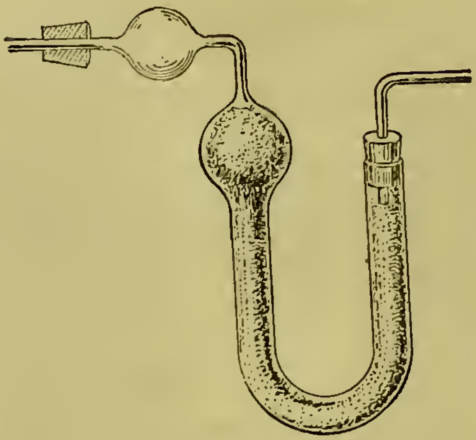


Fig. 29.—Chloride of Calcium Tube.

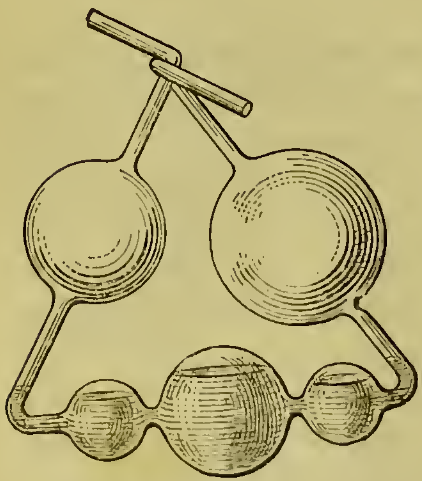
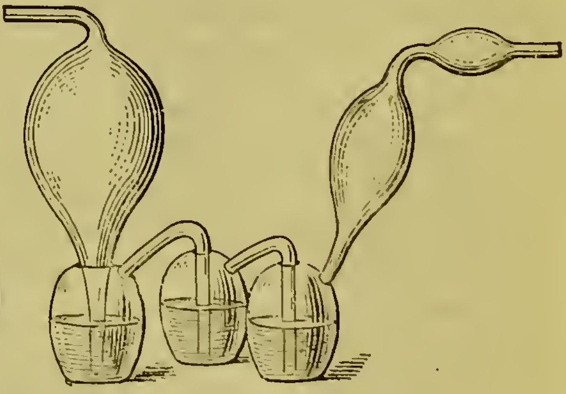


Fig. 30 —Liebig's Potash Bulbs.



Geissler & Mohr's
Potash Bulbs.

weighed calcium chloride tube (E) is then connected to the end of the combustion-tube by means of a perforated cork, and the weighed potash bulbs (Fig. 30) are next connected to the calcium chloride tube at F by means of a small piece of indiarubber tubing; the hinder extremity of the tube at A is connected with a reservoir or gasholder, from which pure dry oxygen can be passed through the apparatus.

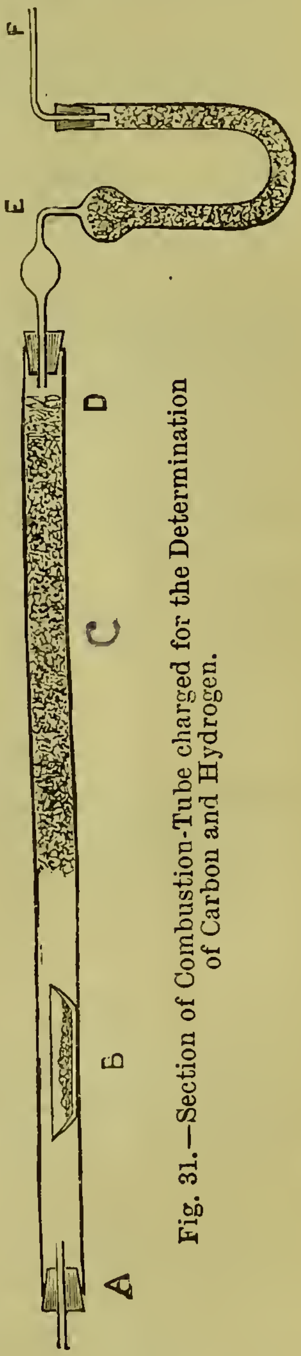


Fig. 31.—Section of Combustion-Tube charged for the Determination of Carbon and Hydrogen.

The fore part of the tube containing the copper oxide is first made red-hot, and oxygen is allowed to pass slowly through the tube; heat is then applied to the part B where the platinum boat containing the sugar has been placed, when the sugar is burnt by the oxygen to carbon dioxide and water, any hydrocarbon vapours that may escape combustion by the oxygen becoming completely oxidised during their transit over the red-hot copper oxide, some of which becomes reduced to cuprous oxide or to metallic copper. The water in the form of aqueous vapour (steam) and the carbon dioxide are carried onwards by the stream of oxygen, the water being entirely absorbed by the calcium chloride, and the carbon dioxide passing on is absorbed by the caustic potash in the potash bulbs. When all the sugar is completely burnt away, and nothing but oxygen bubbles through the potash bulbs, the operation is stopped, and the potash bulbs with the calcium chloride tube are detached and carefully weighed; the increase in weight of the latter gives the amount of water produced, and the increase in weight of the former gives the amount of carbon dioxide produced; from these the actual weights of carbon and hydrogen can easily be calculated. These, then, will be the weights of carbon and hydrogen that were present in the weighed quantity of sugar taken; from which the percentage composition of the sugar can then be calculated.

The following account of a combustion of sugar will serve to demonstrate the method of making these calculations :—

Weight of sugar employed	0·4 gramme.
Weight of potash bulbs after the combustion	52·7425 grammes.
„ „ „ before „	52·1250 „
	·6175 gramme of CO_2 produced.
Weight of calcium chloride tube after the combustion.	33·4895 grammes.
Weight of calcium chloride tube before the combustion.	33·2575 „
	·2320 gramme of H_2O produced.

Now from the calculation of the molecular weight of CO_2,

$$\begin{array}{lr} C & = 12 \\ O_2 = 16 \times 2 & = 32 \\ \hline & 44 \end{array}$$

it is evident that every 44 parts of CO_2 contain 12 parts of C by weight; therefore what weight of C will be contained in ·6175 gramme of CO_2?

$44 : \cdot 6175 :: 12 : x$
$x = \cdot 1684$ gramme of carbon, which is the weight of carbon present in ·4 gramme of sugar.

Similarly, from the calculation of the molecular weight of H_2O,

$$\begin{aligned} H_2 &= 1 \times 2 = 2 \\ O &= 16 \\ &\overline{18} \end{aligned}$$

it is evident that every 18 parts of H_2O contain 2 parts of H by weight; therefore what weight of H will be contained in ·232 gramme of H_2O?

$18 : \cdot 232 :: 2 : x$
$x = \cdot 0257$ gramme of hydrogen, which is the weight of hydrogen present in ·4 gramme of sugar.

If ·4 parts of sugar contain ·1684 parts of carbon, what will 100 parts of sugar contain?

$$\cdot 4 : 100 :: \cdot 1684 : x$$
$$x = 42{\cdot}10 \text{ per cent. of carbon.}$$

If ·4 parts of sugar contain ·0257 parts of hydrogen, what will 100 parts of sugar contain?

$$\cdot 4 : 100 :: \cdot 0257 : x$$
$$x = 6{\cdot}42 \text{ per cent. of hydrogen.}$$

As sugar is composed only of carbon, hydrogen, and oxygen, if the sum of the percentages of carbon and hydrogen be deducted from 100, the difference, viz. 51·48, will represent the percentage of oxygen.

	Percentage composition of sugar as obtained by analysis.	Percentage composition of sugar as obtained by calculation from its formula.
Carbon	42·10	42·11
Hydrogen	6·42	6·43
Oxygen	51·48	51·46
	100·00	100·00

Determination of the carbon and hydrogen in an organic compound containing nitrogen.—The carbon and hydrogen are determined separately from the nitrogen; the process of combustion just described is adopted, but it is necessary to insert in the fore part of the tube at D (Fig. 31) a roll of copper gauze about 3 or 4 inches long; this is made red-hot before commencing the combustion, and reduces any oxides of nitrogen that may be evolved, converting them by abstraction of their oxygen into free nitrogen, which then passes unabsorbed through the calcium chloride tube and potash bulbs, and so escapes. If this were not done, any oxides of nitrogen formed would be absorbed by the caustic potash, and so would vitiate the determination of the carbon.

Determination of the carbon and hydrogen in an organic compound containing chlorine, bromine, or iodine.—Lead chromate should be substituted for the copper oxide, and the combustion proceeded with in the usual manner, the lead chromate keeping back the halogen elements.

Determination of the carbon and hydrogen in an organic liquid.—If it is required to determine the amounts of carbon and hydrogen in an organic liquid, such as alcohol, a bulb is blown on the end of a piece of fine capillary glass tubing, the whole being of about the size shown in Fig. 32, so that it can be easily slipped into the combustion-tube. The bulb is first accurately weighed, it is then warmed over a spirit or Bunsen flame to expand the air within it, and its open end quickly inverted beneath some of the alcohol or whatever organic liquid is being submitted to analysis; as the air in the bulb cools and contracts, the alcohol is forced up into it by atmospheric pressure, and when the bulb is full of alcohol up to A, the end B is inserted for a moment or two into a spirit or Bunsen flame in order to seal it. The sealed bulb is now again weighed, and the increase of weight represents the amount of alcohol contained in it; the sealed end B is then broken off and is placed together with the bulb in the platinum boat (B, Fig. 31), which is then pushed into the combustion-tube, and the combustion proceeded with in the ordinary way, care being taken to apply heat very gradually to the part of the tube under the platinum boat, so that the alcohol shall be slowly converted into vapour, which, carried by the current of oxygen over the red-hot copper oxide, becomes completely oxidised to carbon dioxide and water.

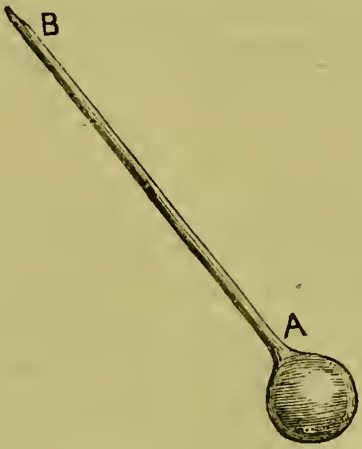


Fig. 32.—Bulb for Weighing Organic Liquids.

Determination of the nitrogen in an organic nitrogenous compound.—The nitrogen of an organic compound is always determined separately from the carbon and hydrogen by a special process. There are three methods in use:—(i) *The soda-lime process*, by which the nitrogen is converted into ammonia, the amount of which is estimated; (ii) *the Kjeldahl process*, in which the substance is heated with strong sulphuric acid and the nitrogen

converted into ammonium sulphate; (iii) *Dumas' method*, by which the nitrogen is evolved in the free state and measured. Before giving the details of these processes it will be convenient to describe how an organic substance is tested so as to ascertain if nitrogen be present. Many substances containing nitrogen, when heated on platinum foil, evolve the
1. smell of burnt feathers; a better test is to heat the body with soda-lime, when most organic bodies con-
2. taining nitrogen evolve ammonia, which can be recognised by the ordinary tests; the most satisfactory method is to heat a small quantity of the
3. substance in a test-tube with a small piece of freshly-cut metallic sodium. When cold the mass is extracted with water, the solution filtered, boiled with a mixture of ferrous sulphate and ferric chloride, and finally rendered acid with hydrochloric acid; if the original substance contained nitrogen, the acid fluid will be dark blue, or yield a blue precipitate. By the action of the sodium, sodium cyanide ($NaCN$) is formed; this, by boiling in the alkaline solution, is converted by the iron salts into sodium ferrocyanide, which, when acidified, gives with the ferric salt Prussian blue.

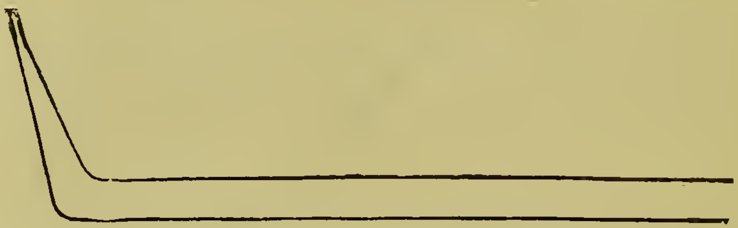


Fig. 33.—Combustion-Tube for the Determination of Nitrogen by the Soda-lime Process.

(i) *The soda-lime process*, or *Will and Varrentrapp's method*.—This process depends upon the fact that if an organic nitrogenous body is heated with a solid caustic alkali, the nitrogen is converted into and is completely evolved as ammonia. A piece of stout combustion-tubing, about 15 inches long, is drawn out to a point at one end, which is bent nearly to a right angle (Fig. 33); the posterior third of this (A, Fig. 34) is filled with the granular soda-lime (a mixture of sodium and calcium hydrates, produced by slaking lime with a strong solution of caustic soda); the weighed quantity of the nitrogenous organic substance is then thoroughly mixed with more soda-lime, and the mixture introduced into the combustion-tube so as to occupy the middle third (B, Fig. 34), the anterior third of the tube is then filled up with soda-lime (C, Fig. 34), in front of which is placed a plug of asbestos, D, to prevent the mechanical carrying over of any of the soda-lime. To the charged combustion-tube is now fitted, by means of a perforated cork, the piece of apparatus, E (Fig. 34), consisting of three bulbs, and containing a measured quantity of dilute sulphuric acid of known strength. Heat is then applied to the fore part of the tube (C and D), and when this has become red-hot the other portions of the tube are gradually heated, until the whole is red-hot. The nitrogen of the organic substance is converted by the soda-lime into ammonia, which as it bubbles through the diluted sulphuric acid contained in the bulbs is absorbed, neutralising some of the sulphuric acid. When no more bubbles pass through the acid the turned-up extremity of the combustion-

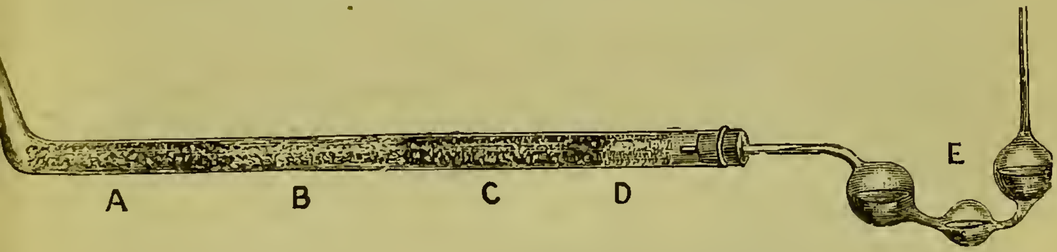


Fig. 34.—Combustion-Tube charged for the Determination of Nitrogen by the Soda-lime Process.

tube is broken off, and air is drawn through the apparatus, so as to displace any ammonia remaining within the combustion-tube into the acid. The bulbs are then withdrawn and the acid turned out into a beaker; the amount of free acid left is determined by seeing what quantity of a standard solution of caustic soda is required to neutralise the acid left unneutralised by the ammonia; the difference between this amount and the amount originally required by the standardised sulphuric acid represents the amount of acid neutralised by the ammonia, from which the amount of ammonia required to neutralise it can easily be calculated. The weight of nitrogen contained in this amount of ammonia then represents the actual weight of nitrogen contained in the weighed quantity of the organic nitrogenous substance operated on, from which the percentage of nitrogen is easily calculated.

(ii) *The Kjeldahl process.*—In this process about 1 gramme of the substance is carefully weighed and placed in a flask holding about 250 c.c., and 20 c.c. of strong sulphuric acid added; the mixture is heated on a sandbath for one hour, nearly to the boiling point, about 8 grammes of dry potassium sulphate in powder are added, and the heating continued till the solution is colourless. When cold an excess of sodium hydrate is added, and the ammonia distilled over and collected in a measured quantity of standard sulphuric acid, as in the previous process (i). The boiling with sulphuric acid converts the nitrogen into ammonium sulphate, which the sodium hydrate decomposes into free ammonia and sodium sulphate.

(iii) *Dumas' method.*—This consists in burning the organic nitrogenous substance with copper oxide, passing the oxides of nitrogen formed over heated metallic copper, to reduce them to nitrogen, and collecting the nitrogen in a graduated tube over a strong solution of caustic potash, which absorbs carbon dioxide, but not nitrogen. Before commencing the combustion, the air within the charged combustion-tube is expelled by means of carbon dioxide. To carry out this process, a piece of combustion-tubing, about 25 inches long, is sealed at one end, test-tube fashion; at the closed end some sodium bicarbonate, A (Fig. 35), is introduced, then some copper oxide, B, then the mixture of copper oxide and the weighed quantity of the organic nitrogenous substance, C; after this some more copper oxide, D, and finally a roll of metallic copper gauze, E. A piece of bent tubing, dipping beneath the surface of mercury in a pneumatic trough, is then connected to the charged combustion-tube by means of a perforated cork. Before the graduated tube F is placed over the delivery tube, heat is applied to the sodium bicarbonate at A, so that the carbon dioxide evolved shall chase out all the air in the combustion and delivery tubes. When this is effected, the heat is removed from the end A, the graduated tube F is filled two-thirds with

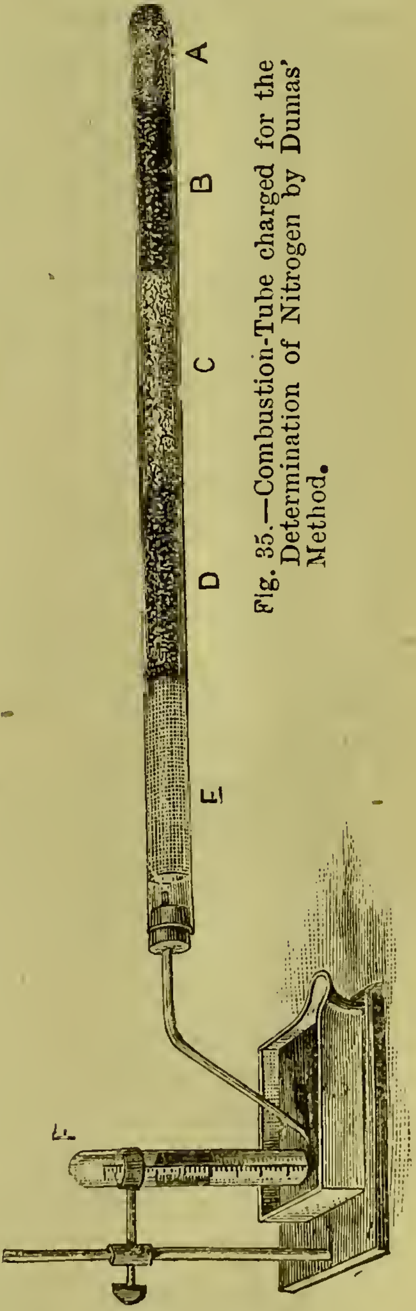


Fig. 35.—Combustion-Tube charged for the Determination of Nitrogen by Dumas' Method.

mercury and one-third with a strong solution of caustic potash, and inverted over the end of the delivery tube—that is, beneath the surface of the mercury in the trough. The combustion is carried on by first making the fore part of the combustion-tube at E red-hot, and gradually extending the heat to the hinder part till it is red-hot throughout. Any oxides of nitrogen formed are reduced by the metallic copper to free nitrogen, which, along with carbon dioxide, bubbles up through the mercury and caustic potash in the graduated tube, the carbon dioxide being completely absorbed by the caustic potash, and the nitrogen only collecting. When the nitrogen ceases to be evolved, the end A of the tube is again heated, so as to evolve carbon dioxide, which expels any nitrogen remaining in the combustion-tube. The volume of nitrogen is then read off, from which the weight can be calculated, and this represents the actual weight of nitrogen that was present in the weighed quantity of the organic nitrogenous body operated on.

Determination of chlorine in organic compounds.—A weighed quantity of the organic compound is heated with pure quicklime (CaO) in a combustion-tube, by which means the chlorine of the organic compound is converted into calcium chloride; the contents of the tube are then dissolved in water and nitric acid, and silver nitrate added to precipitate all the chlorine as silver chloride, which is collected, washed, dried, and weighed. From the weight of silver chloride the amount of chlorine present is calculated, and this will be the actual amount of chlorine present in the weighed quantity of the organic compound operated on.

Iodine and *bromine* in organic compounds are estimated in a precisely similar manner.

Determination of sulphur in organic

compounds.—A weighed quantity of the organic compound is heated in a sealed tube with fuming nitric acid for two hours, by which means the sulphur is oxidised to sulphuric acid; the contents of the tube are boiled with water, and filtered; to the filtrate barium nitrate is added to precipitate the sulphuric acid as barium sulphate, which is collected, washed, dried, and weighed. From the weight of barium sulphate the amount of sulphur present is calculated.

Phosphorus in organic compounds is oxidised to phosphoric acid in a similar manner, and is precipitated as the magnesium ammonium phosphate.

CALCULATION OF THE FORMULA OF AN ORGANIC COMPOUND FROM THE PERCENTAGE COMPOSITION.

The percentage composition represents the proportions of the elements in the compound by weight; as a formula represents the proportions of the elements in atoms. Since the atoms of different elements have different weights, to change the proportions by weight into proportions by atoms, it will be necessary to divide the percentage weights of the elements by their respective atomic weights. The procedure is best demonstrated by taking an example; that of acetic acid will be taken.

The percentage composition of acetic acid is:

Carbon	40·00
Hydrogen	6·66
Oxygen	53·34
	100·00

These proportions of the elements by weight are divided by their respective atomic weights to find their relative proportions as atoms.

Carbon 40·00 ÷ 12 = 3·33
Hydrogen 6·66 ÷ 1 = 6·66
Oxygen 53·34 ÷ 16 = 3·33

The numbers representing the atomic proportions are then, by a common divisor, reduced to the simplest possible whole numbers. It is obvious that in the present case 3·33 is a common divisor, giving the proportions of 1 atom of carbon to 2 atoms of hydrogen and 1 atom of oxygen, which, represented as a formula, is:

$$CH_2O.$$

This is the *empirical formula* of acetic acid; that is, it is the simplest possible expression of its composition, representing the elements of which it is composed, and their relative proportions in atoms to one another. A *molecular formula* indicates the number of atoms in the molecule of a body, and may be the same as the empirical formula, or some simple multiple of it. To ascertain the molecular formula of acetic acid, its vapour-density must be taken; that is, it must be converted into vapour, and the specific gravity of its vapour determined. The molecular weight is obtained by doubling the vapour-density, since the specific gravity of any gas or vapour is half its molecular weight (*see* page 43); it can then be easily ascertained whether this molecular weight is the same as that calculated from the empirical formula, or some multiple of it.

Now, the vapour-density of acetic acid is 30 (that is, its vapour is 30 times heavier than hydrogen at the same temperature and pressure), therefore the molecular weight of acetic acid is 60. The formula CH_2O only gives a weight of 30.

$$\begin{array}{llr} C & & = 12 \\ H_2 & = 1 \times 2 & = 2 \\ O & & = 16 \\ \hline & & 30 \end{array}$$

Therefore, the double of the empirical formula, viz $C_2H_4O_2$, must be the molecular formula of acetic acid since it yields the molecular weight of acetic acid viz. 60.

$$\begin{array}{llr} C_2 & = 12 \times 2 & = 24 \\ H_4 & = 1 \times 4 & = 4 \\ O_2 & = 16 \times 2 & = 32 \\ \hline & & 60 \end{array}$$

A constitutional or rational formula indicates not only the number of atoms in the molecule of a body, but also the way in which those atoms are arranged; that is, it exhibits the constitution or architecture of the body. A constitutional formula can only be arrived at by a series of experiments, which may require to be very elaborate, and the description of which would be out of place here; in fact, the constitution of many organic bodies has not yet been ascertained.

In the case of acetic acid, it is found that out of the four atoms of hydrogen one can be displaced by metals, and therefore must be differently placed to the other three; this may be expressed by a constitutional formula represented thus:

$$HC_2H_3O_2,$$

which indicates the different position of the hydrogen atom that can be displaced by metals, and also shows the grouping of the remaining atoms together to form the *acetic radicle*, $C_2H_3O_2$.

acetates.

It is also found, as the result of experiments, that the three hydrogen atoms are present in acetic acid as a methyl group, CH_3; this may be expressed by a constitutional formula represented thus:

$$\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COHO,}\end{array}\right.$$

which shows that acetic acid is composed of the radicle *methyl* (CH_3) united with the radicle *oxatyl* (COHO).

This formula is confirmed by the action of phosphorus pentachloride. This substance may be said to be a test for the group HO in a compound; whenever a substance contains this hydroxyl group, phosphorus pentachloride expels it from the molecule, and its place is taken by an atom of chlorine.

Acetic acid accordingly, when acted upon by PCl_5, yields $\left\{\begin{array}{l}\mathrm{CH_3}\\ \mathrm{COCl}\end{array}\right.$ (acetyl chloride).

DETERMINATION OF MOLECULAR WEIGHT.

As it is evident that the determination of the molecular weight of an organic substance is most important, it will be convenient here to consider the various methods by which the molecular weight of a substance can be determined. As a rule, purely chemical methods are not sufficient to determine the molecular weight, and we have to rely on two physical methods—(i) the *determination of the specific gravity of the substance in the state of gas or vapour*, often referred to as its *vapour-density*; and (ii) *the depression produced in the freezing-point of a solvent by a known weight of the substance.* Of these the first, the determination of the vapour-density, is by far the most important.

The specific gravity of a substance in the state of gas or vapour can be ascertained either (*a*) by finding the weight of a known volume of the vapour at a known temperature and pressure, or (*b*) by finding the volume occupied by a known weight of the substance when converted into gas or vapour. As an example of "*a*" we may cite Dumas' method. In this a glass bulb (containing about 200 c.c.), furnished with a long drawn-out neck, is partially filled with the substance the specific gravity of whose vapour is to be determined. The bulb is then plunged into a heated liquid, so that the substance boils violently, and its vapour drives out all the air from the bulb. When this has been effected and the bulb is full of the vapour, the end of the drawn-out neck is fused up by a blowpipe, the temperature of the heated liquid and the barometer being simultaneously noted. The bulb is then withdrawn, cleaned, and weighed. The weight of the empty bulb is deducted, and thus we get the weight of a known volume of the vapour at a known temperature and pressure: from this, after certain corrections, we can calculate the specific gravity of the vapour at 0° and 760 mm. (For full details, *see*

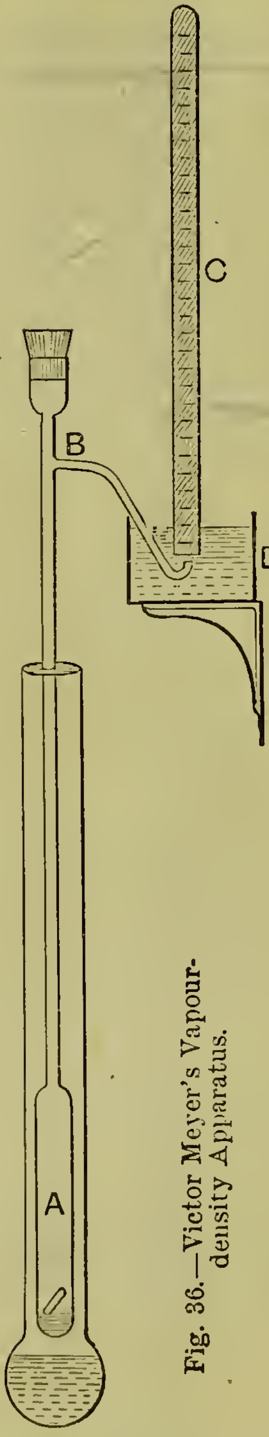


Fig. 36.—Victor Meyer's Vapour-density Apparatus.

"Quantitative Analysis," Clowes and Coleman, page 421.)

The method which is, however, usually employed belongs to the second class, "*b*." It is known as Victor Meyer's method. A tube about two feet long is expanded at its lower end into a bulb A (Fig. 36); it is closed at its upper end with an india-rubber cork, and has a short delivery tube B inserted a short distance below the cork; the delivery tube ends in a trough D filled with water. The bulbed tube A is surrounded by a second and larger tube which contains water, anilin, or other liquid of suitable boiling-point. This liquid is caused to boil, and its vapour heating the air in A causes it to expand and bubbles escape by the delivery tube into the air. As soon as bubbles cease to escape, the cork is removed and a weighed quantity of the substance contained in a small bulb (*see* Fig. 32) is dropped into A, and the cork immediately replaced. The substance is at once converted into vapour, which displaces some of the air, and this displaced air is collected in the graduated tube C, which has been placed over the end of the delivery tube. The liquid in the outer tube should have a boiling-point 20° to 30° higher than that of the substance; about 0·1 grm. of the substance should be taken.

The volume of the gas collected is corrected for temperature, pressure, etc., to 0° and 760 mm. The weight of this volume of hydrogen is then calculated and divided into the weight of substance taken. As an example: ·073 gramme of ether displaced 25·3 c.c. of air, measured at 21·5° C., and pressure 718·6 mm., correcting for temperature.

$$25{\cdot}3 \times \frac{273}{273 + 21{\cdot}5} = 23{\cdot}45 \text{ c.c.}$$

the pressure was 718·6 – 19·1 (the vapour tension of water at 21·5) = 699·5 mm.

$$23{\cdot}45 \times \frac{699{\cdot}5}{760} = 21{\cdot}5 \text{ c.c.}$$

the volume of gas displaced when reduced to 0° C. and 760 mm.

Now this volume of hydrogen weighs

$$\frac{21{\cdot}5 \times {\cdot}0896}{1{,}000} = {\cdot}00192,$$

and the specific gravity of ether vapour equals

$$\frac{{\cdot}073}{{\cdot}00192} = 37{\cdot}9.$$

The second method, that of determining the molecular weight by the depression of the freezing-point, is generally carried out in an apparatus invented by Beckmann. It consists of a stout glass vessel A (Fig. 37), which contains cold water, ice, or ice and salt, according as glacial acetic acid, benzene, or water is used as the solvent. In this is fixed a large test-tube B, furnished with a wide side tube C, which is closed by a cork. The upper end of the tube B is also closed by a cork, through which pass a delicate thermometer D, divided into $\frac{1}{100}$ths of a degree, and a platinum wire E, bent at its lower end to form a stirrer. The lower end of B is surrounded by an empty tube F, which serves as an air-jacket, and ensures a *gradual* change of temperature. A known weight of the solvent (usually water or glacial acetic acid) is introduced into the tube B, which is then immersed in the cooling vessel A: the solvent is vigorously stirred, allowed to freeze, and the freezing-point noted. A weighed quantity of the substance is then introduced by the side tube C, and the experiment repeated, the freezing-point being again noted. The difference in temperature between the two observations gives the lowering of the freezing-point produced by a given weight of the substance.

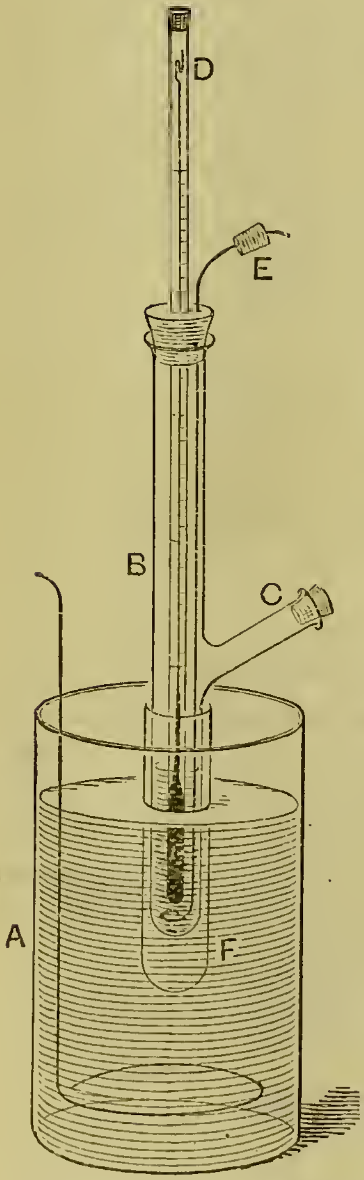


Fig. 37.—Beckmann's Apparatus for Determining the Depression of the Freezing-point.

Now, Raoult and others have shown that if a *molecular weight* of a substance in grammes is dissolved in 100 grammes of a suitable solvent, the depression of the freezing-point produced is always—within certain limits—the same, *whatever the nature of the substance.* This depression is therefore a constant for any one solvent; for water it is 19, for glacial acetic acid 39. It is denoted by the letter K. It has also been proved that if the solution is dilute, *the depression produced is proportional to the weight of the substance dissolved;* thus, if one gramme of a substance dissolved in 100 grammes of a solvent produces a depression of ·06°, two grammes will produce a depression twice as great, ·12, etc. So if one gramme be dissolved in 100 grammes of the solvent, then the observed depression $(D) = K \times \frac{1}{\text{molecular weight}}$, K being the depression produced by a molecular weight in grammes. Similarly, if G grammes be used,

$$D = \frac{K \times G}{M.\,W.} \quad \text{or} \quad M.\,W. = \frac{K \times G}{D}$$

As an example, 13·68 grammes of dextrose were dissolved in 100 grammes of water, and produced a depression of 1·45°.

$$\text{Molecular weight} = \frac{19 \times 13{\cdot}68}{1{\cdot}45} = 179{\cdot}9.$$

The molecular weight calculated for $C_6H_{12}O_6 = 180$.

ISOMERIC BODIES.

The term *isomeric* (from ἴσος, equal; μέρος, part) is applied to those bodies that have the same percentage composition, but which differ in their properties. In other words, isomeric bodies are composed of the same elements, and in the same proportions, but yet they are entirely different bodies, as indicated by their entirely different properties. These different properties are due to a different arrangement of the atoms in the molecules of isomeric bodies; so that although isomeric bodies have the same composition, they have a different constitution. For instance, oil of turpentine and oil of lemons are isomeric bodies; they both possess the formula $C_{10}H_{16}$, yet they differ markedly in their properties, and this difference is due to different arrangements of the atoms in their respective molecules; although the atoms, or chemical bricks, out of which two substances are constructed are the same, yet the architecture of their molecules is entirely different.

Isomeric bodies are generally divided into two groups—(1) those the members of which have the same molecular weight, and which are called simply *isomeric bodies*; (2) those the members of which, whilst having the same percentage composition, yet differ in molecular weight, and which are called *polymeric bodies* (from πολύς, many, and μέρος, part).

As examples of *isomeric bodies* may be mentioned: urea $CO\left\{\begin{array}{l}NH_2\\NH_2\end{array}\right.$ and ammonium isocyanate(NH_4NCO); ordinary ether $(C_2H_5)_2O$, and methyl propyl ether (CH_3, C_3H_7, O); propionic acid $\left\{\begin{array}{l}CH_3\\CH_2\\COOH\end{array}\right.$; methyl acetate $\left\{\begin{array}{l}CH_3\\COOCH_3\end{array}\right.$, and ethyl formate $\left\{\begin{array}{l}H\\COOC_2H_5\end{array}\right.$; oil of turpentine $(C_{10}H_{16})$ and oil of lemons $(C_{10}H_{16})$. As examples of polymeric bodies, acetylene (C_2H_2) and benzene (C_6H_6); cyanogen $(CN)_2$ and paracyanogen $(CN)_n$).

gr
2
52 mo. wt.
26 = sp. gr.

CHAPTER III

CYANOGEN GROUP.

Cyanogen—Potassium Ferrocyanide—Potassium Cyanide—Hydrocyanic Acid—Tests for Hydrocyanic Acid and Cyanides—Potassium Ferricyanide—Methyl Cyanide—Ethyl Cyanide—Potassium Cyanate—Ammonium Cyanate—Potassium Sulphocyanate—Urea.

C_2N_2

Cy.

Cyanogen (C_2N_2).—The name cyanogen (from *κύανος, blue; γεννάω, to generate*) is due to the fact that some of the double cyanogen compounds possess brilliant blue colours.

Preparation of cyanogen.—Cyanogen is a gas, and is obtained by heating either mercuric cyanide or silver cyanide.

Heating

$$\underset{\text{Mercuric cyanide.}}{Hg(CN)_2} = \underset{\text{Mercury.}}{Hg} + \underset{\text{Cyanogen.}}{(CN)_2}$$

$$\underset{\text{Silver cyanide.}}{2AgCN} = \underset{\text{Silver.}}{2Ag} + \underset{\text{Cyanogen.}}{(CN)_2}$$

Properties of cyanogen.—Cyanogen is a
1. colourless gas, possessing a peculiar odour somewhat
2. resembling that of the essential oil of bitter almonds;
3. it is soluble in water, and is very poisonous. It burns
4. with a characteristic coloured flame, the colour re-
5. sembling that of the peach blossom, and it produces
6. carbon dioxide and free nitrogen when burnt. Its
specific gravity is 26, and it is therefore much heavier than air; its molecular weight is 52, and its formula $(CN)_2$. CN is often written Cy.

Tests for cyanogen.—The odour of the gas, combined with the peculiar colour of its flame when ellow Prussiate of Potash.

burnt, constitute the best means for the recognition of cyanogen.

Potassium ferrocyanide (K_4FeCy_6).—This body is the ancestor of the cyanogen compounds. Since no cyanogen compounds exist in nature, it is necessary that one or more of them should be made by some artificial process, and the cyanogen compound that is prepared artificially is potassium ferrocyanide. To prepare this substance it is necessary to employ some potassium salt to furnish the potassium, the metal iron to furnish the iron, and some organic substance, rich in carbon and nitrogen, to furnish the elements for the production of the cyanogen. It is made, therefore, by roasting together potassium carbonate, iron filings, and animal matter, such as hoofs, horns, and scraps of hide, substances that are rich in both carbon and nitrogen. Under the influence of the heat, and in presence of the other substances, the carbon and nitrogen unite to form cyanogen, which, with the potassium carbonate, forms potassium cyanide (KCy), and with the iron forms ferrous cyanide ($FeCy_2$). On boiling the melted mass with water, these two cyanides unite to form potassium ferrocyanide.

Ke

KC

$$\underset{\text{Potassium cyanide.}}{4KCy} + \underset{\text{Ferrous cyanide.}}{FeCy_2} = \underset{\text{Potassium ferrocyanide.}}{K_4FeCy_6}$$

Properties.—Potassium ferrocyanide occurs in yellow crystals, and is commonly known as *yellow prussiate of potash*. Although the powerful poisons hydrocyanic acid and potassium cyanide are made from it, yet potassium ferrocyanide itself is non-poisonous. It is decomposed when strongly heated with production of potassium cyanide and carbide of iron. Potassium ferrocyanide is decomposed by both strong and dilute sulphuric acid, but with different results in the two cases. If heated with strong sulphuric acid, carbon monoxide is copiously evolved.

$$\underset{\text{Potassium ferrocyanide.}}{K_4Fe(CN)_6} + \underset{\text{Sulphuric acid.}}{6H_2SO_4} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Potassium sulphate.}}{2K_2SO_4} +$$

$$\underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Ammonium sulphate.}}{3(NH_4)_2SO_4} + \underset{\text{Carbon monoxide.}}{6CO}$$

If heated with dilute sulphuric acid, hydrocyanic acid only is evolved.

$$\underset{\text{Potassium ferrocyanide.}}{2K_4FeCy_6} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} = \underset{\text{Hydrocyanic acid.}}{6HCy} +$$

$$\underset{\text{Ferro-potassium ferrocyanide.}}{FeK_2FeCy_6} + \underset{\text{Potassium sulphate.}}{3K_2SO_4}$$

Potassium ferrocyanide is used in the manufacture of *Prussian blue*, which is ferric ferrocyanide ($Fe_4(FeCy_6)_3$), and which is prepared by adding potassium ferrocyanide to a solution of ferrous sulphate. The precipitate thus obtained is oxidised with dilute nitric acid or chlorine water.

Tests.—(i) Potassium ferrocyanide gives with a solution of ferric chloride a dark blue precipitate.

(ii) A solution of copper sulphate gives with potassium ferrocyanide a reddish-brown precipitate of copper ferrocyanide. This is a most delicate test for the salt.

(iii) Potassium ferrocyanide heated with dilute sulphuric acid evolves the odour of hydrocyanic acid.

Potassium cyanide (KCy).—This salt is prepared in the form of commercial cyanide of potassium used for photographic purposes, and also as the pure cyanide of potassium. The commercial cyanide of potassium may be prepared by strongly heating potassium ferrocyanide (*see* page 364), but it is most conveniently prepared at a lower temperature by fusing together potassium ferrocyanide and potassium carbonate. The cyanide of potassium prepared by this process is, however, always mixed with some cyanate.

$$\underset{\text{Potassium ferrocyanide}}{K_4FeCy_6} + \underset{\text{Potassium carbonate.}}{K_2CO_3} = \underset{\text{Potassium cyanide.}}{5KCy} + \underset{\text{Potassium cyanate.}}{KCyO} + \underset{\text{Iron.}}{Fe} + \underset{\text{Carbon dioxide}}{CO_2}$$

Pure cyanide of potassium may be prepared by neutralising hydrocyanic acid with caustic potash; this is most conveniently effected by passing the vapour of hydrocyanic acid into an alcoholic solution of caustic potash, when the potassium cyanide crystallises out as it is formed.

$$\underset{\text{Hydrocyanic acid.}}{HCy} + \underset{\text{Caustic potash.}}{KHO} = \underset{\text{Potassium cyanide.}}{KCy} + \underset{\text{Water.}}{H_2O}$$

Potassium cyanide may also be prepared by utilising the nitrogen of the air. This is effected by passing air over a mixture of potassium carbonate and charcoal strongly heated, when potassium cyanide is formed and carbon monoxide evolved.

Properties. — Potassium cyanide is a white crystalline solid, evolving, on exposure to the air, the odour of hydrocyanic acid. It is very poisonous and is readily acted on by acids, hydrocyanic acid being evolved. Both strong and dilute sulphuric acid decompose it, evolving hydrocyanic acid.

$2KCy$	+	H_2SO_4	=	$2HCy$	+	K_2SO_4
Potassium cyanide.		Sulphuric acid.		Hydrocyanic acid.		Potassium sulphate.

Potassium cyanide is a powerful reducing substance, thus when heated with litharge it forms metallic lead and potassium cyanate.

Tests.—The tests for potassium cyanide are the same as those for hydrocyanic acid (*see* page 369).

Hydrocyanic acid (HCN or HCy).—This acid is commonly known as *prussic acid*, on account of its first having been prepared from Prussian blue; it may be prepared from potassium ferrocyanide or from any metallic cyanide. The hydrocyanic acid used in medicine (*Acidum hydrocyanicum dilutum*) is prepared by distilling potassium ferrocyanide with dilute sulphuric acid (*see* page 365), and diluting the distillate to the required strength. It may also be prepared by shaking together solutions of potassium cyanide and tartaric acid, when the potassium acid tartrate is deposited on standing, leaving the hydrocyanic acid in solution.

KCy	+	$H_2C_4H_4O_6$	=	HCy	+	$KHC_4H_4O_6$
Potassium cyanide.		Tartaric acid.		Hydrocyanic acid.		Potassium acid tartrate.

Pure hydrocyanic acid, which is seldom prepared on account of its extremely poisonous nature and the danger incurred by the operator in the preparation of it, may be obtained by passing dried sulphuretted hydrogen gas over heated mercuric cyanide, the hydrocyanic acid vapour being condensed in a suitable apparatus surrounded by a freezing mixture.

HgCy~

$HgCy_2$	+	H_2S	=	$2HCy$	+	HgS
Mercuric cyanide.		Sulphuretted hydrogen.		Hydrocyanic acid.		Mercuric sulphide.

Hydrocyanic acid is present in the *essential oil of bitter almonds*, being produced from the decomposition of the glucoside amygdalin under the influence of the ferment emulsin present in the bitter almonds, the presence of water being necessary for the emulsin to act on the amygdalin. 4.

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Oil of bitter almonds.}}{C_7H_6O} + \underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

Properties.—Hydrocyanic acid is an extremely powerful and rapidly acting poison; only a very dilute solution of it is employed in medicine, the Diluted Hydrocyanic Acid, B. P., being of only 2 per cent. strength. If dilute hydrocyanic acid be kept for some time with exposure to light it slowly decomposes, becoming converted into ammonium formate. 2

$$\underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Ammonium formate.}}{NH_4CHO_2}$$

Hydrocyanic acid is contained in essential oil of bitter almonds, essence of peach kernels, essence of cherry kernels, bitter almond water and cherry laurel water. The strength of a sample of hydrocyanic acid can be determined by ascertaining the weight of silver cyanide precipitated by adding an excess of silver nitrate solution to a known quantity of the diluted hydrocyanic acid. The antidote, in cases of poisoning by hydrocyanic acid, is to convert the soluble and diffusible hydrocyanic acid into the insoluble Prussian blue. This is effected by giving a draught containing a mixture of sodium carbonate, ferrous sulphate, and ferric chloride. The sodium carbonate forms sodium cyanide.

$$\underset{\text{Hydrocyanic acid.}}{2HCy} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} = \underset{\text{Sodium cyanide.}}{2NaCy} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon dioxide.}}{CO_2}$$

This, with the ferrous sulphate, forms sodium ferrocyanide:

$$\underset{\text{Sodium cyanide.}}{6NaCy} + \underset{\text{Ferrous sulphate.}}{FeSO_4} = \underset{\text{Sodium ferrocyanide.}}{Na_4FeCy_6} + \underset{\text{Sodium sulphate}}{Na_2SO_4}$$

and this, with the ferric chloride, forms Prussian blue.

$$\underset{\text{Ferric chloride.}}{4FeCl_3} + \underset{\text{Sodium ferrocyanide.}}{3Na_4FeCy_6} = \underset{\text{Prussian blue.}}{Fe_4(FeCy_6)_3} + \underset{\text{Sodium chloride.}}{12NaCl}$$

As a matter of fact, hydrocyanic acid is so rapid in its action as a poison, that, as a rule, there is not time to obtain and administer so complex an antidote as the one just described.

Tests for hydrocyanic acid.—(i) *Prussian blue test.*—This consists in adding to the hydrocyanic acid, caustic soda, solution of ferrous sulphate, solution of ferric chloride, heating, and then acidifying with hydrochloric acid. The first three reagents act as described in connection with the antidote (*see* above); the hydrochloric acid is finally added to neutralise any excess of caustic alkali, which would, if present, prevent the development of the Prussian blue.

(ii) *Sulphocyanide test.*—This depends on the conversion of the hydrocyanic acid into ferric sulphocyanide, which is of a deep blood-red colour. This conversion is effected by adding to the hydrocyanic acid solution of ammonia and then a few drops of yellow ammonium sulphide, and evaporating the mixture to a low bulk; to the concentrated liquid, hydrochloric acid and ferric chloride are then added, when the deep blood-red colour of ferric sulphocyanide is produced. The solution of ammonia converts the hydrocyanic acid into ammonium cyanide.

$$\underset{\text{Hydrocyanic acid.}}{HCy} + \underset{\text{Ammonia.}}{NH_3} = \underset{\text{Ammonium cyanide.}}{NH_4Cy}$$

The free sulphur contained in the yellow ammonium sulphide then converts this ammonium cyanide into ammonium sulphocyanide.

$$\underset{\text{Ammonium cyanide.}}{NH_4Cy} + \underset{\text{Sulphur.}}{S} = \underset{\text{Ammonium sulphocyanide.}}{NH_4CyS}$$

This sulphocyanide, on the addition of ferric chloride, forms the blood-red ferric sulphocyanide. The hydrochloric acid is merely added to neutralise any excess of ammonia that may be present, which would otherwise prevent the formation of the ferric sulphocyanide.

$$\underset{\text{Ferric chloride.}}{FeCl_3} + \underset{\text{Ammonium sulphocyanide.}}{3NH_4CyS} = \underset{\text{Ferric sulphocyanide.}}{Fe(CyS)_3} + \underset{\text{Ammonium chloride.}}{3NH_4Cl}$$

In some respects the cyanides resemble the chlorides, both giving a white curdy precipitate with silver nitrate. In the case of the cyanide, the precipitate is soluble in excess of the cyanide.

Potassium ferricyanide (K_3FeCy_6). — This is prepared from potassium ferrocyanide by raising the iron from the ferrous state, in which it exists in the ferrocyanide, into the ferric state, in which it exists in the ferricyanide; this is most conveniently effected by passing chlorine into a solution of potassium ferrocyanide.

$$\underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{2K_4FeCy_6} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Potassium}\\\text{ferrieyanide.}}}{2K_3FeCy_6} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{2KCl}$$

Properties.—Potassium ferricyanide occurs in reddish-brown crystals, and is commonly known as *red prussiate of potash.* With a solution of a ferrous salt potassium ferricyanide gives a dark blue precipitate. With ferric salts it gives no precipitate at all, but merely a dark olive-green colour, and hence it is readily distinguished from potassium ferrocyanide, which with ferric chloride gives a dark blue precipitate. It is a powerful oxidising substance.

ALCOHOLIC CYANIDES.

Methyl cyanide (CH_3CN). — This alcoholic cyanide is prepared by distilling the potassium salt of methyl sulphuric acid with potassium cyanide.

$$\underset{\substack{\text{Potassium}\\\text{methyl sulphate.}}}{KCH_3SO_4} + \underset{\substack{\text{Potassium}\\\text{cyanide.}}}{KCN} = \underset{\substack{\text{Methyl}\\\text{cyanide.}}}{CH_3CN} + \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4}$$

Ethyl cyanide (C_2H_5CN).—This is prepared in a similar manner to the above by distilling the potassium salt of ethyl sulphuric acid with potassium cyanide.

$$\underset{\substack{\text{Potassium}\\\text{ethyl sulphate.}}}{KC_2H_5SO_4} + \underset{\substack{\text{Potassium}\\\text{cyanide.}}}{KCN} = \underset{\substack{\text{Ethyl}\\\text{cyanide.}}}{C_2H_5CN} + \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4}$$

Potassium sulphocyanate or sulphocy-

anide (KCNS).—This may be prepared by fusing together potassium ferrocyanide and sulphur.

$$\underset{\text{Potassium ferrocyanide.}}{K_4FeCy_6} + \underset{\text{Sulphur.}}{6S} = \underset{\text{Potassium sulphocyanide.}}{4KCyS} + \underset{\text{Ferrous sulphocyanide.}}{Fe(CyS)_2}$$

The fused mass is then boiled with water and potassium carbonate added to convert the ferrous sulphocyanide into potassium sulphocyanide and ferrous carbonate, the latter being precipitated.

$$\underset{\text{Ferrous sulphocyanide.}}{Fe(CyS)_2} + \underset{\text{Potassium carbonate.}}{K_2CO_3} = \underset{\text{Potassium sulphocyanide.}}{2KCyS} + \underset{\text{Ferrous carbonate.}}{FeCO_3}$$

The soluble sulphocyanides may also be prepared by direct union of the soluble cyanides and sulphur, as in the sulphocyanide test for hydrocyanic acid (*see* page 369). Potassium sulphocyanide is present in minute quantities in the saliva of man.

Test.—Potassium sulphocyanide gives with ferric chloride a deep blood-red colour. This colour is not discharged on the addition of strong hydrochloric acid; it is thus distinguished from the blood-red colour given by ferric chloride with an acetate, the colour of ferric acetate being discharged by strong hydrochloric acid (*see* page 434). The colour of ferric sulphocyanide is discharged on the addition of a solution of mercuric chloride, and in this way it is distinguished from the blood-red colour given by ferric chloride with meconic acid or a meconate, the red colour of ferric meconate not being discharged by mercuric chloride (*see* Chapter XI., Alkaloids).

CYANATES AND UREA.

Potassium cyanate (KCNO).—This may be prepared by exposing fused potassium cyanide for

some time to the air, when oxygen is absorbed and 1,
the cyanate formed; or it may be prepared by 2
dropping a metallic oxide, such as lead oxide, into the fused potassium cyanide; the latter unites with the oxygen of the lead oxide, forming potassium cyanate, and the metal lead is set free.

Ammonium cyanate (NH_4CNO).—This salt is prepared by mixing solutions of potassium cyanate and ammonium sulphate, when double decomposition takes place.

$$\underset{\text{Potassium cyanate.}}{2KCNO} + \underset{\text{Ammonium sulphate.}}{(NH_4)_2SO_4} = \underset{\text{Ammonium cyanate.}}{2NH_4CNO} + \underset{\text{Potassium sulphate.}}{K_2SO_4}$$

Alcohol is then added to precipitate the potassium sulphate, leaving the ammonium cyanate in solution. This salt is of interest as its isomer *urea* ($CO(NH_2)_2$) can be prepared from it. The conversion of ammonium cyanate into urea is effected by simply evaporating its solution to dryness on the water-bath, when urea is left; the temperature of boiling water is therefore sufficient to change ammonium cyanate into urea. The urea, in its turn, may be reconverted into ammonium cyanate by raising it to a dull red heat, when ammonia gas is evolved and cyanuric acid formed.

$$\underset{\text{Urea.}}{3CO(NH_2)_2} = \underset{\text{Cyanuric acid.}}{H_3C_3N_3O_3} + \underset{\text{Ammonia.}}{3NH_3}$$

If the cyanuric acid be more strongly heated, it splits up into cyanic acid, which distils over.

$$\underset{\text{Cyanuric acid.}}{H_3C_3N_3O_3} = \underset{\text{Cyanic acid.}}{3HCNO}$$

If the cyanic acid is neutralised with ammonia, ammonium cyanate is reproduced.

$O(NH_2)_2$

As urea is so closely connected with ammonium cyanate, it will be convenient to consider it here, although it belongs to a group of bodies, the amides, whose structure has not yet been studied (*see* p. 383).

Urea or **carbamide** ($CO(NH_2)_2$).—This important amide occurs as a normal constituent of urine, it being the chief form in which the waste or superfluous nitrogen of the system is eliminated. As an amide, it is derived from two molecules of ammonia by displacement of two out of the six atoms of hydrogen by the bivalent radicle carbonyl (CO); thus:

$$N_2\left\{\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right. \qquad\qquad N_2\left\{\begin{matrix}CO\\H_2\\H_2\end{matrix}\right.$$

Ammonia (2 molecules). Urea or carbamide.

The formula and constitution of urea are more conveniently represented by showing the bivalent carbonyl radicle (CO) in direct union with two equivalents of amidogen (NH_2); thus:

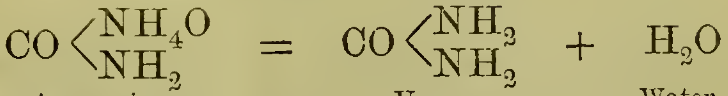
$$CO\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.$$

Preparation.—(i) Urea may be extracted from urine by evaporating the urine to one-sixth of its bulk, and adding, when cold, strong nitric acid; on standing, yellowish crystals of the nitrate of urea are deposited; these are collected on a filter, dissolved in boiling water, and barium carbonate added to form barium nitrate and free urea. The whole is then evaporated to dryness on a water-bath, and the dry residue exhausted with boiling alcohol, which dissolves out the urea, leaving the barium nitrate insoluble;

the filtered alcoholic solution, when evaporated, deposits crystals of urea.

(ii) Urea may be prepared from its isomer ammonium cyanate by simply evaporating a solution of that salt to dryness on a water-bath (*see* page 373).

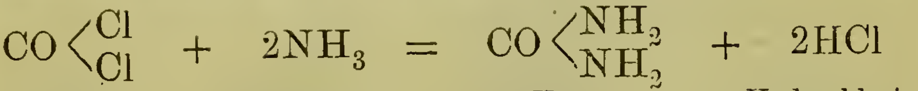
(iii) Urea is obtained by heating ammonium carbamate ($NH_4NH_2CO_2$), so as to deprive it of the elements of water.



$$\underset{\text{Ammonium carbamate.}}{CO\left\langle\begin{matrix}NH_4O\\NH_2\end{matrix}\right.} = \underset{\text{Urea.}}{CO\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.} + \underset{\text{Water.}}{H_2O}$$

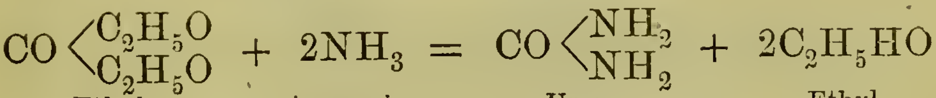
[illegible] Car.

(iv) Urea can also be obtained by the action of ammonia on carbonyl chloride ($COCl_2$). (*See* page 162.)



$$\underset{\text{Carbonyl chloride.}}{CO\left\langle\begin{matrix}Cl\\Cl\end{matrix}\right.} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Urea.}}{CO\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{2HCl}$$

(v) Urea is also produced by acting on ethyl carbonate ($(C_2H_5)_2CO_3$) with ammonia.



$$\underset{\text{Ethyl carbonate.}}{CO\left\langle\begin{matrix}C_2H_5O\\C_2H_5O\end{matrix}\right.} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Urea.}}{CO\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.} + \underset{\text{Ethyl alcohol.}}{2C_2H_5HO}$$

Properties.—Urea occurs in transparent colourless crystals, soluble in water and alcohol; under the influence of heat it evolves ammonia, producing at first biuret, then cyanuric acid, and finally cyanic acid (*see* p. 373). Urea is neutral to test paper, but if urine is exposed to the air it soon becomes alkaline (owing to the action of bacteria), from conversion of the urea into ammonium carbonate, which is formed by the union of urea with the elements of water.

$$\underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Ammonium carbonate.}}{(NH_4)_2CO_3}$$

Urea is instantaneously decomposed by nitrous acid, carbon dioxide and nitrogen being evolved.

$$\underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\text{Nitrous acid.}}{2HNO_2} = \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Nitrogen.}}{2N_2} + \underset{\text{Water.}}{3H_2O}$$

It is also decomposed by the hypobromites and hypochlorites with evolution of carbon dioxide and nitrogen; thus sodium hypobromite (NaBrO) in presence of urea is reduced to sodium bromide (NaBr), its oxygen oxidising the carbon and hydrogen of the urea to carbon dioxide and water respectively, the nitrogen being set free.

$$\underset{\text{Urea.}}{CO(NH_2)_2} + \underset{\text{Sodium hypobromite.}}{3NaBrO} = \underset{\text{Sodium bromide.}}{3NaBr} + \underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Nitrogen.}}{N_2} + \underset{\text{Water.}}{2H_2O}$$

Estimation of urea in urine.—*Hypobromite process.*—This process consists in decomposing the urea in a measured quantity of urine by means of sodium hypobromite, an excess of free caustic soda being present in the hypobromite solution, so that the carbon dioxide is absorbed by it, and only the nitrogen is evolved; the volume of nitrogen evolved is then measured. The apparatus (Fig. 38) consists of a bottle A, into which 25 c.c. of a strong alkaline solution of sodium hypobromite are introduced; into this is carefully lowered a small test-tube *b* containing 5 c.c. of the urine to be examined, care being taken not to spill any of the urine into the hypobromite solution. The bottle A is then connected by means of a perforated cork and india-rubber tubing with the graduated tube B, which is immersed in a reservoir of water C; before the commencement of each experiment, the water in B is adjusted so as to be at the zero mark.

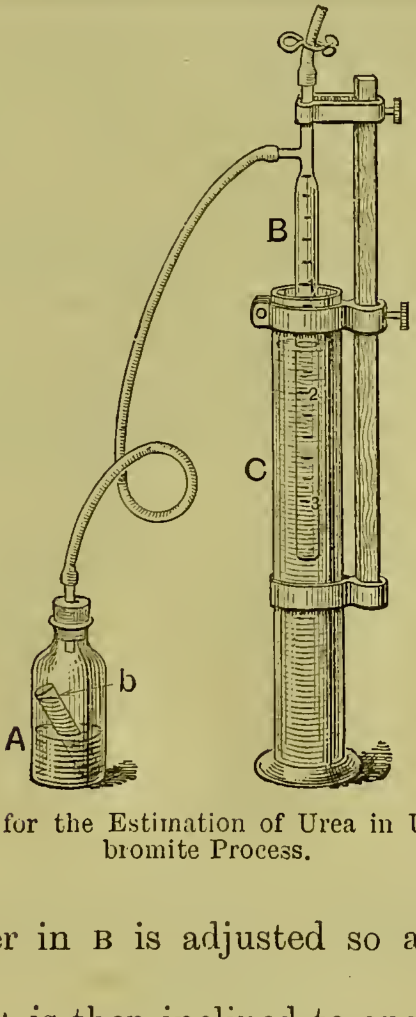


Fig. 38.—Apparatus for the Estimation of Urea in Urine by the Hypobromite Process.

The bottle A is then inclined to one side, so as to allow the urine contained in the small tube *b* to flow into the hypobromite solution, when the urea is immediately decomposed into carbon dioxide, nitrogen, and water; the carbon dioxide is instantly absorbed by the caustic soda present in the solution, and only the nitrogen escapes with effervescence. Whatever the amount of nitrogen evolved, there will be an equal volume of the air contained in the apparatus forced over into the measuring tube B, where the amount can be read off, after cooling, by lowering B into the water in C and then raising B until the liquids in B and C are at the same level, and from its volume the amount of urea contained in the 5 c.c. of urine can be determined. Employing 5 c.c. of urine in connection with each estimation, the tube B is so graduated that the numbers 1, 2, 3, etc., marked on it represent 1, 2, and 3 per cent. of urea in the urine.

Tests.—A solution of urea gives (i) a white precipitate with a solution of mercuric nitrate.

(ii) An effervescence of nitrogen with an alkaline solution of sodium hypobromite.

(iii) If moderately strong, crystals of urea nitrate, when mixed in the cold with strong nitric acid.

CHAPTER IV.

CLASSIFICATION OF ORGANIC COMPOUNDS.

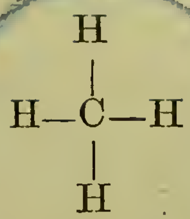
THE following are the chief groups of organic compounds, with illustrations of each :—

Hydrocarbons.—Compounds of carbon and hydrogen only. A very large number of hydrocarbons exist ; the most important are the following : (*a*) *paraffins*, (*b*) *olefines*, (*c*) *acetylene series*, (*d*) *benzene or aromatic series.*

Paraffins, on account of being completely saturated bodies, have but little affinity for other elements, hence the derivation of their name (from *parum affinis*, little affinity) ; olefines derive their name from olefiant gas or ethene (C_2H_4), the first known member of the group of unsaturated hydrocarbons.

All paraffins are referable to the general formula CnH_{2n+2}, that is, by doubling the number of the carbon atoms, and adding two, the number of the hydrogen atoms will always be obtained. The simplest *paraffin* is methane or marsh gas (CH_4).

methane



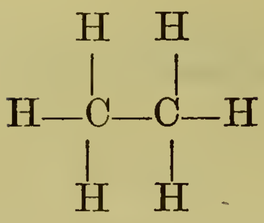
$$\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H \end{array}$$

CH4

Graphic formula of methane.

The two carbon *paraffin* is ethane (C_2H_6).

Ethane



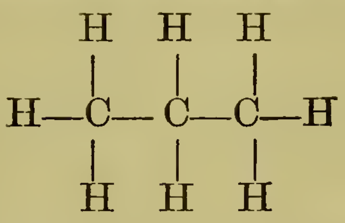
$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & H & \end{array}$$

C_2H_6

Graphic formula of ethane.

The three-carbon *paraffin* is propane (C_3H_8).

Propane

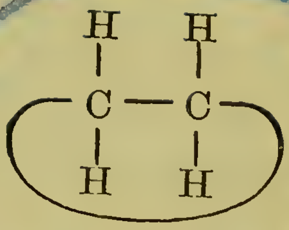


$$\begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -H \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$

C_3H_8

Graphic formula of propane.

The simplest *olefine* is ethene or olefiant gas (C_2H_4). The graphic formula shows that two of the atom-fixing powers of the carbon atoms are not united with hydrogen, but these, when the olefine is in the free state, unite with one another, and so neutralise their fixing powers.



Graphic formula of ethene.

It will be seen that the three paraffins just mentioned, CH_4, C_2H_6, C_3H_8, constitute a series, any member of which differs from the succeeding one by CH_2; such a series, the members of which differ in composition by a constant quantity, which have similar reactions and show a regular gradation of physical properties, such as boiling point, melting point, etc., is called a *homologous series.*

Alcohols.—The hydrates or hydroxides of hydrocarbon radicles; the *monatomic alcohols* are the hydrates of univalent hydrocarbon radicles: *e.g.* methyl alcohol (CH_3HO) and ethyl alcohol (C_2H_5HO); the *diatomic alcohols* are the hydrates of bivalent hydrocarbon radicles; *e.g.* ethylene glycol ($C_2H_4(HO)_2$); the *triatomic alcohols* are the hydrates of trivalent hydrocarbon radicles; *e.g.* glycerine ($C_3H_5(HO)_3$); and so on.

OH

Aldehydes.—Compounds derived from alcohols by the abstraction of two atoms of hydrogen from the molecule of an alcohol, *e.g.*—

— H_2

Ethyl alcohol	C_2H_6O.
Ethyl aldehyde	C_2H_4O.

They are generally produced by the gentle oxidation of the alcohols; they all contain the group (COH), thus the formula of ~~acetic~~ aldehyde may be written $\left\{\begin{matrix}CH_3\\COH\end{matrix}\right.$ as ethyl alcohol may be written $\left\{\begin{matrix}CH_3\\CH_2OH\end{matrix}\right.$

COH

Ethers.—The oxides of hydrocarbon radicles. As alcohols are the hydrates of hydrocarbon radicles, so to every alcohol there is a corresponding ether, the ether being the oxide of the radicle of which the alcohol is the hydrate: *e.g.*—

O

Methyl alcohol	$CH_3.HO$.	Ethyl alcohol	$C_2H_5.HO$.
Methyl ether	$(CH_3)_2.O$.	Ethyl ether	$(C_2H_5)_2.O$.

Ethereal salts or esters.—Compounds of the hydrocarbon or alcohol radicles with acid radicles. An ethereal salt may be regarded as derived from an alcohol the hydroxyl of which has been displaced by a negative radicle: *e.g.*—

+ ac radic

Ethereal Salts. = Comps. of alc radicles with acid radicles

Ethyl nitrite or nitrous ether $C_2H_5.NO_2$,
Ethyl acetate or acetic ether $C_2H_5C_2H_3O_2$;

just as we derive from potassium hydrate by a similar replacement, potassium nitrite, KNO_2, etc.

If the negative radicle united with the alcohol radicle is one of the halogen elements (chlorine, bromine, iodine, fluorine), then the ethereal salt is sometimes called a *haloid ether* : *e.g.*—

Methyl chloride $CH_3.Cl$.
Ethyl iodide C_2H_5I.

Organic acids.—Compounds containing the radicle oxatyl or carboxyl (COOH) united usually with some other radicle. The substance united with the oxatyl may be simply hydrogen, as in the case of formic acid, or it may be an alcohol radicle, as in the case of acetic acid, or it may be oxatyl itself, as in the case of oxalic acid.

$$\left\{\begin{matrix}\mathrm{H}\\ \mathrm{COOH}\end{matrix}\right. \qquad \left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COOH}\end{matrix}\right. \qquad \left\{\begin{matrix}\mathrm{COOH}\\ \mathrm{COOH}\end{matrix}\right.$$

Formic acid. Acetic acid. Oxalic acid.

The basicity of the acid (*see* page 36) depends upon the number of oxatyl (COOH) groups the acid contains; if it contains one such group, as in acetic acid, it is monobasic; if two, as in oxalic acid, it is dibasic, etc.

It is instructive also to notice that the acids may be looked upon as the hydrates of oxidised radicles. Thus, $(C_2H_5)HO$ is ordinary alcohol; if we replace two atoms of hydrogen in the ethyl by one of oxygen we have the oxidised radicle *acetyl* (C_2H_3O), and the hydrate of this $((C_2H_3O)HO)$ is acetic acid.

Anhydrides.—These may be regarded as the acids deprived of water, or as the oxides of the oxidised radicles, just as the ethers are the oxides of the hydrocarbon radicles, thus:

$$\underset{\text{Acetic acid.}}{2\left\{\begin{matrix}CH_3\\COOH\end{matrix}\right.} \quad - \quad \underset{\text{Water.}}{H_2O} \quad = \quad \underset{\text{Acetic anhydride.}}{\begin{pmatrix}CH_3\\CO\end{pmatrix}_2 O}$$

Acetic anhydride can also be written $(C_2H_3O)_2O$, just as ethyl ether is written $(C_2H_5)_2O$.

Acid halides are the chlorides and other salts of the oxidised radicles, thus $(C_2H_3O)Cl$, acetyl chloride, etc.

Ketones.—These bodies in some respects resemble the aldehydes, but they contain the group COR (where R may be any organic radicle), instead of the group COH, thus $\left\{\begin{matrix}CH_3\\COCH_3\end{matrix}\right.$, acetone.

Amines.—Bodies derived from ammonia (NH_3) by replacing one or more atoms of hydrogen by an organic radicle, thus:

NH_2CH_3 Methylamine.
$N(CH_3)_3$ Trimethylamine.

They closely resemble ammonia in their reactions and properties.

Amides.—Bodies derived from ammonia by replacing one or more atoms of hydrogen by the acid or oxidised radicles, thus:

$NH_2(C_2H_3O)$ Acetamide.
$\left.\begin{matrix}NH_2\\NH_2\end{matrix}\right\} CO$ Carbamide or urea.

The amides can also be looked upon as acids in which HO groups have been replaced by amidogen

(NH_2); thus, in carbonic acid $\left(CO\begin{cases}OH\\OH\end{cases}\right)$, if we replace the two HO groups, we have $CO\begin{cases}NH_2\\NH_2\end{cases}$ urea. The amides are usually neutral bodies uniting both with acids and bases.

Organo-metallic bodies in which the radicles are combined with metals, as $Zn(C_2H_5)_2$, zinc ethyl.

Organic bodies containing sulphur, selenium, etc., instead of oxygen, as sulphur alcohol or mercaptan (C_2H_5HS).

$$\text{Sulphur urea } CS\begin{cases}NH_2,\\NH_2,\end{cases}$$

or **phosphorus or arsenic,** instead of nitrogen, as kakodyl $(As_2(CH_3)_4)$.

methyl
ethyl
propyl
butyl

CHAPTER V.

30

HYDROCARBONS.

Paraffin or Fatty Series—Occurrence in Nature—Methane—Ethane—Petroleum—Olefine Series—Ethylene—Acetylene Series—Acetylene—Coal Gas—Structure of Flame.

The paraffin hydrocarbons may be looked upon as the hydrogen compounds or hydrides of the radicles methyl, etc., thus, marsh gas or methane ($(CH_3)H$), ethane ($(C_2H_5)H$), etc.

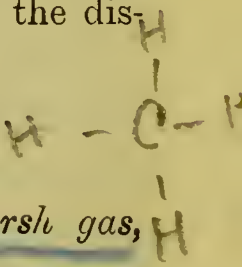
It is a most important series; all members have the formula C_nH_{2n+2}. About thirty members are known; the first four are gases. Pentane (C_5H_{12}) and all the members up to $C_{17}H_{36}$ are liquids, the rest being solids. 30

They are all *saturated* bodies—*i.e.* none of the bonds of the carbon atoms are latent. The strongest acids and the most powerful alkalies fail to attack them. When mixed with chlorine and exposed to light, the hydrogen atoms can be replaced by chlorine.

Their occurrence in nature is interesting. In 1847 a small petroleum spring in a Derbyshire coal mine was discovered by the late Lord Playfair; this was purified and used for illuminating purposes. It soon, however, became exhausted, and in 1850 Young obtained a similar oil by distilling a hard slaty coal. This industry still continues in Scotland. Soon after (in 1859) a bore hole was made in search of petroleum at Titusville, in America, and a spring was struck yielding 800 gallons a day. Since that date numerous springs have been discovered in America, Russia, and elsewhere.

Crude petroleum or, as it is called in this country, "fractional distillation."

paraffin oil, is a mixture of many paraffins and a small quantity of olefines. The latter are destroyed by agitation with strong sulphuric acid, the acid neutralised by soda, and the oil distilled in fractions, which are separated according to their boiling points. Thus, the most volatile portion, boiling 40°—70°, is known as petroleum ether; that boiling 70°—90° as gasoline; light petroleum, or benzoline, comes over at 80°—120°. Then we have the portion boiling 120°—170°, which is sometimes used as a substitute for turpentine; next come the ordinary burning oils, known as "paraffin" or kerosene, boiling 150°—300°. Above these we have lubricating oils, vaseline, and various tarry substances; and, in the distillate from shale, paraffin wax.



(I.) PARAFFIN SERIES.

Methane (CH_4).—Known also as *marsh gas, fire-damp*, and *light carburetted hydrogen.*

Modes of preparation.—(i) By heating a mixture of sodium acetate and caustic soda, the latter being most conveniently employed in the form of soda-lime.

$$NaC_2H_3O_2 + NaHO = CH_4 + Na_2CO_3$$

Sodium acetate.	Sodium hydrate.	Methane.	Sodium carbonate.

(ii) By passing a mixture of sulphuretted hydrogen and the vapour of carbon disulphide over red-hot copper.

$$2H_2S + CS_2 + 8Cu = CH_4 + 4Cu_2S$$

Sulphuretted hydrogen.	Carbon disulphide.	Copper.	Methane.	Cuprous sulphide.

(iii) Methane is produced by the slow decomposition of vegetable substances, as in marshes and

Saturated [illegible]

stagnant pools, when it is known as *marsh gas;* it is also found in coal mines, where it is known as *fire-damp.* It issues from the earth in enormous volumes in certain localities, the Crimea, Pittsburg, etc.

(iv) Methane is formed by the dry or destructive distillation of various organic substances, and is one of the chief constituents of coal gas (about 34 per cent.).

(v) Marsh gas can also be produced by the action of water upon aluminium carbide (Al_4C_3).

Properties of methane.—A colourless, inodorous, and tasteless gas, condensing to a liquid at – 164°.

Its specific gravity is 8, and it is therefore much lighter than air; it is but very slightly soluble in water, and is combustible, but not a supporter of combustion. It burns with a feebly luminous flame, producing carbon dioxide and water; if mixed with oxygen or air, and a light applied to the mixture, an explosion will take place; this is the chief cause of the disastrous explosions that occur in coal mines. Methane is not poisonous, but it is incapable of supporting life. A mixture of methane and excess of chlorine exposed to bright sunshine explodes, forming hydrochloric acid and setting free carbon; but in diffused daylight chlorine acts upon methane slowly and quietly, forming a series of substitution products according to the amount of chlorine used. Thus, if equal volumes of methane and chlorine are employed, methyl chloride or monochlormethane (CH_3Cl) is formed.

$$\underset{\text{Methane.}}{CH_4} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Methyl}\\\text{chloride.}}}{CH_3Cl} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl}$$

If 1 volume of methane and 2 volumes of chlorine are employed, bichloride of methylene or dichlormethane (CH_2Cl_2) is formed.

$$\underset{\text{Methane.}}{CH_4} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Methylene bichloride.}}{CH_2Cl_2} + \underset{\text{Hydrochloric acid.}}{2HCl}$$

If 1 volume of methane and 3 volumes of chlorine are employed, chloroform or trichlormethane ($CHCl_3$) is formed.

$$\underset{\text{Methane.}}{CH_4} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Chloroform.}}{CHCl_3} + \underset{\text{Hydrochloric acid.}}{3HCl}$$

Lastly, if 1 volume of methane and 4 volumes of chlorine are employed, carbon tetrachloride or tetrachlormethane (CCl_4) is formed.

$$\underset{\text{Methane.}}{CH_4} + \underset{\text{Chlorine.}}{4Cl_2} = \underset{\text{Carbon tetrachloride.}}{CCl_4} + \underset{\text{Hydrochloric acid.}}{4HCl}$$

Test for methane.—The formation of chloroform by the exposure of a mixture of 1 volume of the gas and 3 volumes of chlorine to diffused daylight constitutes the best test for methane.

4/6

Ethane (C_2H_6).—This paraffin may be considered as di-methyl $(CH_3)_2$, or ethyl hydride $(C_2H_5)H$, and may be obtained by the action of sodium on a solution of methyl iodide in ether.

$$\text{(i)}\quad \underset{\text{Methyl iodide.}}{2CH_3I} + \underset{\text{Sodium.}}{2Na} = \underset{\text{Ethane.}}{C_2H_6} + \underset{\text{Sodium iodide.}}{2NaI}$$

(ii) By electrolysis of sodium or potassium acetate.

$$\underset{\text{Potassium acetate.}}{2KC_2H_3O_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Ethane.}}{C_2H_6} + \underset{\text{Potassium bicarbonate.}}{2HKCO_3} + \underset{\text{Hydrogen.}}{H_2}$$

In its properties it resembles methane.

gases having same density CO C_2H_4 } =1

(II.) OLEFINE SERIES.

Ethylene (C_2H_4).—Known also as *ethene*, *olefiant gas*, and *heavy carburetted hydrogen*.

Modes of preparation.—(i) By heating a mixture of one volume of alcohol and four volumes of strong sulphuric acid. The action of the sulphuric acid is simply that of dehydration, or withdrawal of the elements of water from the alcohol; the temperature of the mixture must be above 154°.

$$\underset{\text{Alcohol.}}{C_2H_6O} - \underset{\text{Water.}}{H_2O} = \underset{\text{Ethylene.}}{C_2H_4}$$

(ii) By passing acetylene (C_2H_2) through a mixture of zinc and an alkali generating nascent hydrogen.

$$\underset{\text{Acetylene.}}{C_2H_2} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Ethylene.}}{C_2H_4}$$

(iii) Ethylene is produced during the dry or destructive distillation of many organic bodies—coal, for instance—and is present to the amount of about 2 to 5 per cent. in coal gas.

Properties of ethylene.—A colourless, inodorous, and tasteless gas; its specific gravity is 14, and it is therefore a little lighter than air liquefies at, – 103°; it is very slightly soluble in water, and is combustible, but not a supporter of combustion. It burns with a very luminous flame, producing carbon dioxide and water; the luminosity of coal gas when burnt is in great part due to the presence of ethylene in the gas. A mixture of ethylene and oxygen or air explodes on the application of a light. Ethylene is not a direct poison, but it is incapable of supporting life. It unites with chlorine, bromine, and iodine, forming oily liquids, and hence its old name of olefiant gas (from *oleum*, oil, and *fians*, forming); its compound with chlorine, ethylene chloride ($C_2H_4Cl_2$), was discovered by some Dutch chemists, and is known as *Dutch liquid.* Ethylene dissolves in strong sulphuric acid forming ethylsulphuric acid.

$$\underset{\text{Ethylene.}}{C_2H_4} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Ethylsulphuric}\\ \text{acid.}}}{HC_2H_5SO_4}$$

This, when boiled with water, splits up into alcohol and sulphuric acid.

$$\underset{\substack{\text{Ethylsulphuric}\\ \text{acid.}}}{HC_2H_5SO_4} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Ethyl}\\ \text{alcohol.}}}{C_2H_5HO} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{H_2SO_4}$$

Ethylene is the simplest member of the olefine series of hydrocarbons; they have the general formula C_nH_{2n}, the first four members are gases, the next fourteen liquids. They are unsaturated bodies, so that chlorine and bromine *add* themselves on directly, as in the formation of Dutch liquid.

Tests for ethylene. — The luminosity with which the gas burns, combined with its being inodorous, and the fact that it forms an oily liquid with chlorine, and is absorbed by strong sulphuric acid, constitute the best means for the identification of this gas.

Propylene (C_3H_6).—This olefine may be prepared by heating propyl iodide (C_3H_7I) with an alcoholic solution of caustic potash.

$$\underset{\substack{\text{Propyl}\\ \text{iodide.}}}{C_3H_7I} + \underset{\substack{\text{Caustic}\\ \text{potash.}}}{KHO} = \underset{\text{Propene.}}{C_3H_6} + \underset{\substack{\text{Potassium}\\ \text{iodide.}}}{KI} + \underset{\text{Water.}}{H_2O}$$

H ✓

(III.) ACETYLENE SERIES.

Acetylene (C_2H_2).—This body is of interest in that it is the only hydrocarbon that can be prepared by direct union of its elements.

Modes of preparation.—(i) By synthesis; if the electric arc is produced in an atmosphere of hydrogen, the two elements will unite at the very high temperature produced, and about 9 per cent. of acetylene is formed.

$$\underset{\text{Carbon.}}{2C} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Acetylene.}}{C_2H_2}$$

(ii) By passing the vapour of chloroform over red-hot copper.

$$\underset{\text{Chloroform.}}{2CHCl_3} + \underset{\text{Copper.}}{6Cu} = \underset{\text{Acetylene.}}{C_2H_2} + \underset{\text{Cuprous chloride.}}{3Cu_2Cl_2}$$

(iii) By the incomplete combustion of ethylene (C_2H_4), as when the coal gas in a Bunsen burner catches fire at the bottom of the burner; on account of the insufficient supply of air under such conditions, only part of the hydrogen of the ethylene undergoes combustion, acetylene being produced.

$$\underset{\text{Ethene.}}{2C_2H_4} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Acetylene.}}{2C_2H_2} + \underset{\text{Water.}}{2H_2O}$$

(iv) By the action of water on calcium carbide.

$$\underset{\text{Calcium carbide.}}{CaC_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Acetylene.}}{C_2H_2} + \underset{\text{Calcium hydrate.}}{Ca(HO)_2}$$

Of late years this method has been largely used for making acetylene for illuminating purposes; 1 lb. of carbide yields about 5 cubic feet of nearly pure acetylene. Care should be taken in its use. It should not be subjected to a pressure of more than two atmospheres. The calcium carbide (made by heating chalk with charcoal in the electric furnace) should be free from phosphide, or hydrogen phosphide may be produced and fire the acetylene.

Properties of acetylene.—A colourless gas, possessing an unpleasant odour; its specific gravity is 13. It burns with a very bright and (unless the burner has a very small orifice) smoky flame, on account of the large amount of carbon contained in it; if mixed with chlorine it explodes almost instantly.

COAL GAS.

Coal gas is a mixture of gases, consisting mainly of hydrogen and hydrocarbons, produced by the dry or destructive distillation of coal. The coal is heated, without contact of air, in iron retorts, and the products of its destructive distillation are made to pass, firstly, through condensers in which, as a result of the cooling they are subjected to, the heavy coal-tar and the lighter ammoniacal gas-liquor are condensed and collected in tanks; and, secondly, the gas is led through towers filled with wet coke to dissolve out the ammonia, and then through purifying chambers, containing either moist slaked lime or ferric oxyhydrate spread on shelves, either of which removes the gaseous impurities containing sulphur, the former removing carbon dioxide as well; finally, the gas is stored in a gasometer.

The constituents of coal gas may be divided into three groups—the *diluents*, *illuminants*, and *impurities*. The *diluents* are gases which, without conferring much luminosity on coal gas when burnt, yet serve the important purpose of diluting down the heavy hydrocarbons, which by themselves would yield a smoky flame; they constitute about 90 per cent. by volume of the coal gas. The *illuminants* are hydrocarbon gases or vapours rich in carbon, and to their presence the luminosity of coal gas when burnt is due; they constitute about 5 per cent. by volume of the coal gas. The *impurities* consist of nitrogen derived from a little air getting into the retorts when opened for the purpose of recharging, and of some carbon dioxide, ammonia, and traces of sulphur compounds which may have escaped removal in the purifiers.

Composition of coal gas.—

		By volume.
Diluents	Hydrogen	52 per cent.
	Methane or marsh gas	34 ,, ,,
	Carbonic oxide	6 ,, ,,
Illuminants	Ethylene or olefiant gas Acetylene Benzene vapour	4 ,, ,,
Impurities	Nitrogen Ammonia Carbon disulphide vapour, etc. Carbon dioxide	4 ,, ,,

STRUCTURE OF GAS OR CANDLE FLAME.

A gas or candle flame consists of three layers (Fig. 39)—an outer or colourless layer, A, consisting of completely burnt gases; a middle or luminous layer, B, consisting of partially-burnt gases, and containing floating in it minute particles of carbon; and an inner or colourless layer, C, consisting of unburnt gases.

Taking the gas flame by way of illustration, in the outer layer A, both the hydrogen and the carbon of the gaseous constituents are completely oxidised by the oxygen of the air to water and carbon dioxide; to the middle layer, B, only a limited supply of oxygen from the air can gain access, most of it being used up in the outer layer; the hydrocarbons are therefore only partially burnt, and some particles of carbon (or dense hydrocarbon vapours) which are set free are rendered incandescent by the heat of the flame, and so emit the white light to which the luminosity of the flame is due. The presence of free carbon in the middle layer can be demonstrated by inserting a piece of white porcelain into the flame, when the carbon is deposited on it as soot or lamp-black. The inner layer of the flame must necessarily consist of unburnt gas, since as there is insufficient oxygen reaching the middle layer for the complete combustion of its constituents, none can gain access to the inner layer. If air is introduced with the gas from within the flame, as in the Bunsen burner, then complete combustion of both the hydrogen and the carbon of the gas occurs, and the result is the colourless Bunsen flame.

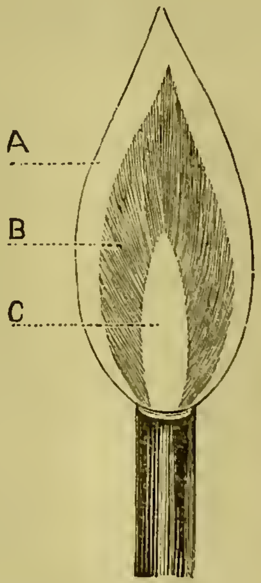


Fig. 89.—Structure of Gas or Candle Flame.

The temperature of a gas flame is very high in an ordinary flat flame burner, about 1370°; a Bunsen flame is about 1500°. According to some observers, the luminosity of a gas flame is caused by the decomposition of the ethylene into marsh gas and carbon when the particles of the latter become incandescent. The enormous economy in the consumption of gas effected by the Welsbach incandescent burner is due to the fact that the 86 per cent. of hydrogen and marsh gas, which in an ordinary burner produces practically no light, is utilised in the incandescent burner to heat up and thus render luminous the infusible mantle.

atomic = C_2H_5-OH Ethyl

Diatomic = $C_2|H_4(OH)_2$ Ethylene Gly

Triatomic = $C_3H_5(OH)_3$ Glycerin

CHAPTER VI.

ALCOHOLS AND THEIR DERIVATIVES.

1. Monohydric Alcohols—Methyl Alcohol—Methyl Compounds—Ethyl Alcohol—Ethyl Compounds—Ether—Chloral—Chloroform—Iodoform—Propyl Alcohol—Butyl Alcohol—Amyl Alcohol—2. Dihydric Alcohols—Ethylene Glycol—3. Trihydric Alcohols—Glycerin.

1. MONOHYDRIC ALCOHOLS.

THESE are the hydrates of the univalent hydrocarbon radicles, and therefore contain in the molecule only one hydroxyl group. They are therefore analogous to such bodies as potassium hydrate (KHO), etc., but they differ from such substances in having very feeble basic properties; they do, however, combine with acids to form salts or esters, as CH_3Cl, methyl chloride, $(CH_3)_2SO_4$, methyl sulphate, etc., just as potassium hydrate combines with hydrochloric acid to form potassium chloride and water. The alcohols of principal medical importance are those containing the radicles (C_nH_{2n+1}) homologous with methyl.

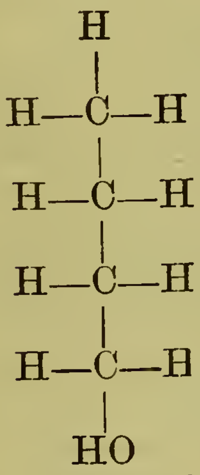
The principal members of this series are:

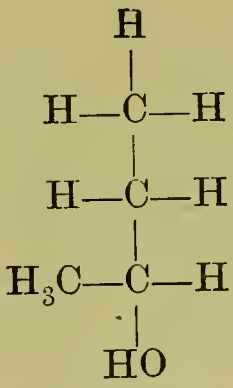
Methyl	alcohol	CH_3HO.
Ethyl	,,	C_2H_5HO.
Propyl	,,	C_3H_7HO.
Butyl	,,	C_4H_9HO.
Amyl	,,	$C_5H_{11}HO$.

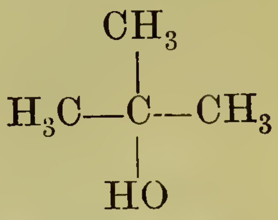
Another nomenclature for these alcohols is that of designating methyl alcohol as *carbinol*, and the alcohols formed by successive substitution of methyl, ethyl, etc., for an atom of hydrogen in the carbinol, are then named according to the radicles which they contain. Thus:

Carbinol or methyl alcohol	$CH_3.HO.$
Methyl carbinol or ethyl alcohol	$CH_2(CH_3).HO.$
Ethyl carbinol or propyl alcohol	$CH_2(C_2H_5).HO.$
Propyl carbinol or butyl alcohol	$CH_2(C_3H_7).HO.$
Butyl carbinol or amyl alcohol	$CH_2(C_4H_9).HO.$

The graphic formula of butyl alcohol may be constructed in three different ways, according as the carbon atom, in union with the hydroxyl, is directly united with one, two, or three other carbon atoms. These are the primary, secondary, and tertiary butyl alcohols. Thus:


Primary butyl alcohol.


Secondary butyl alcohol.


Tertiary butyl alcohol.

These three alcohols have all been prepared. The primary alcohol boils at 117°, the secondary at 100°, the tertiary at 84°.

Thus, a *primary* alcohol is one in which the carbon atom in union with the hydroxyl is only directly united with one other carbon atom; a *secondary* alcohol is one in which the carbon atom in union with the hydroxyl is directly united with two other carbon atoms; a *tertiary* alcohol is one in which the carbon atom in union with the hydroxyl is directly united with three other carbon atoms.

ALCOHOLS OF THE (C_nH_{2n+1}) OR METHYL SERIES.

METHYL ALCOHOL AND METHYL COMPOUNDS.

Methyl alcohol (CH_3HO).—This alcohol may be prepared from methane or marsh gas (CH_4) by acting on it with chlorine to form methyl chloride (CH_3Cl); if this is decomposed with moist silver oxide, methyl alcohol is produced.

$$\underset{\text{Methyl chloride.}}{2CH_3Cl} + \underset{\text{Silver oxide.}}{Ag_2O} + \underset{\text{Water.}}{H_2O} = \underset{\text{Methyl alcohol.}}{2CH_3HO} + \underset{\text{Silver chloride.}}{2AgCl}$$

Pure methyl alcohol may also be prepared from the *oil of winter green*, which is pure methyl salicylate; by distilling this with caustic potash or soda methyl alcohol is obtained. Impure methyl alcohol, commonly known as *wood spirit or wood naphtha*, is obtained by the dry or destructive distillation of wood (*see* page 433); 10 per cent. of this wood spirit mixed with rectified spirit formerly constituted the *methylated spirit* of commerce. The present methylated spirit contains coal tar spirit, which renders it useless for many purposes in the laboratory.

Properties.—Methyl alcohol is a colourless, inflammable liquid; it produces carbon dioxide and water when burnt. In the pure state it is free from the disagreeable smell possessed by wood spirit. Methyl alcohol is converted by oxidation into formaldehyde, and then into formic acid; this oxidation may be effected either by dropping methyl alcohol on to platinum black, the occluded oxygen

$H_3OH + O_2 =$ co-o-H.

of which oxidises the alcohol, or by distillation with potassium bichromate and sulphuric acid.

CH_3HO	$+$	O_2	$=$	$\begin{cases} H \\ COOH \end{cases}$	$+$	H_2O
Methyl alcohol.		Oxygen.		Formic acid.		Water.

The test for methyl alcohol is to convert it by the last-mentioned process into formic acid (for the detection of which *see* page 431).

Methyl chloride (CH_3Cl).—This may be prepared by exposing equal volumes of methane and chlorine to sunlight (*see* page 388). It may also be prepared by the action of phosphorous chloride on methyl alcohol.

$3CH_3HO$	$+$	PCl_3	$=$	$3CH_3Cl$	$+$	H_3PO_3
Methyl alcohol.		Phosphorous chloride.		Methyl chloride.		Phosphorous acid.

Methyl iodide (CH_3I).—This is prepared by the action of phosphorous tri-iodide on methyl alcohol.

$3CH_3HO$	$+$	PI_3	$=$	$3CH_3I$	$+$	H_3PO_3
Methyl alcohol.		Phosphorous iodide.		Methyl iodide.		Phosphorous acid.

Methyl oxide or **methyl ether** ($(CH_3)_2O$).—This is prepared by heating a mixture of equal volumes of methyl alcohol and strong sulphuric acid, when it passes over as a colourless gas.

Methyl sulphuric acid (HCH_3SO_4).—This is prepared by the action of sulphuric acid on methyl alcohol, with moderate heat.

Dimethyl-ketone or **acetone** ($CH_3-CO-CH_3$).—This ketone is prepared by the action of dry heat on any metallic acetate.

$\{CH_2\ O-H$.

$$\underset{\substack{\text{Sodium}\\\text{acetate.}}}{2NaC_2H_3O_2} = \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\text{Acetone.}}{CH_3-CO-CH_3}$$

It may also be prepared by the action of sodium methide on carbonyl chloride:

$$\underset{\substack{\text{Carbonyl}\\\text{chloride.}}}{Cl-CO-Cl} + \underset{\substack{\text{Sodium}\\\text{methide.}}}{2NaCH_3} = \underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl} + \underset{\text{Acetone.}}{CH_3-CO-CH_3}$$

All the primary alcohols when oxidised form first, the corresponding aldehydes which pass into the fatty acid containing the same number of carbon atoms. Thus, methyl alcohol $\left(\left\{\begin{matrix}H\\CH_2HO\end{matrix}\right.\right)$ forms $\left(\left\{\begin{matrix}H\\COH\end{matrix}\right.\right)$ formaldehyde, and then $\left(\left\{\begin{matrix}H\\COOH\end{matrix}\right.\right)$ formic acid.

A secondary alcohol when oxidised forms a corresponding ketone, whilst a tertiary alcohol on oxidation splits up into a mixture of ketones and fatty acids.

By the action of metallic sodium upon methyl alcohol, it is found that only one atom of hydrogen can be replaced by sodium. We therefore conclude that one of the atoms of hydrogen is differently combined to the other three. Again, methyl alcohol is produced by the action of potash upon methyl chloride (CH_3Cl). Now, in this last substance the three atoms of hydrogen must be combined with the atom of carbon, so we conclude that they are similarly combined in methyl alcohol, and we write the formula CH_3HO. This is confirmed by the action of phosphorus pentachloride, which replaces one hydroxyl group (which presumably, therefore, exists as such) by chlorine.

ETHYL ALCOHOL AND ETHYL COMPOUNDS.

Ethyl alcohol (C_2H_5HO).—This constitutes the ordinary alcohol of commerce as contained in proof spirit, rectified spirit, absolute alcohol, wines, and beers. It may be prepared by a synthetical process, which is of interest as showing the building up of the alcohol from its elements. To effect this, acetylene is first prepared by direct union of its elements, by the production of the electric arc in an atmosphere of hydrogen; the acetylene (C_2H_2) is then converted into ethylene by nascent hydrogen (sodium amalgam).

$$\underset{\text{Acetylene.}}{C_2H_2} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Ethylene.}}{C_2H_4}$$

The ethylene is then agitated with strong sulphuric acid, which converts it into ethyl sulphuric acid.

$$\underset{\text{Ethylene.}}{C_2H_4} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Ethyl sulphuric}\\\text{acid.}}}{HC_2H_5SO_4}$$

The ethyl sulphuric acid, if distilled with water, yields ethyl alcohol as a distillate.

$$\underset{\substack{\text{Ethyl sulphuric}\\\text{acid.}}}{HC_2H_5SO_4} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5HO} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4}$$

The various forms of ethyl alcohol met with in commerce are obtained by the fermentation of sugar under the influence of the yeast. If a solution of ordinary sugar ($C_{12}H_{22}O_{11}$) is mixed with yeast, and the mixture kept in a covered vessel in a warm place, the cane sugar is first converted into glucose.

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + \underset{\text{Water.}}{H_2O} = \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

A A

The glucose is then decomposed, by the fermentative action of the yeast, into alcohol and carbon dioxide, small quantities of other bodies (such as glycerin, succinic acid, etc.) also being produced.

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\text{Ethyl alcohol.}}{2C_2H_6O} + \underset{\text{Carbon dioxide}}{2CO_2}$$

When the fermentative process is finished, the alcohol is obtained in a weak state from the mixture by distillation. This weak spirit is then strengthened by the process known as *fractional distillation*, which consists in distilling it in portions, the greater quantity of the alcohol being contained in the first distillate. It is not possible to remove all the water by the process of fractional distillation; the strongest spirit that can be so obtained is rectified spirit, which contains 10 per cent. of water. To prepare *absolute alcohol* from this, that is, alcohol quite free from water, the rectified spirit is mixed with freshly-burnt lime, and allowed to stand for some hours in a closed vessel. The lime unites with the water, forming slaked lime, and the pure or absolute alcohol can then be obtained by distillation. In the preparation of malt alcoholic liquors (beer, stout, and porter), the starch contained in barley is converted by a ferment *diastase*, which exists in the barley grain, into a mixture of dextrin and a form of sugar known as *maltose*; the latter is extracted with hot water, and the solution, when sufficiently cold, fermented with yeast. Maltose, unlike cane sugar, is *directly* converted by yeast into alcohol and carbon dioxide.

Properties.—Ethyl alcohol is a colourless liquid with a faint, pleasant smell, and is readily inflammable, producing, when burnt, carbon dioxide and water. *Proof spirit* contains 49 parts by weight of alcohol in 100 volumes, and is of sp. gr. 0·920. *Rectified spirit* contains 90 parts by volume in 100 volumes of alcohol' and is of sp. gr. 0·834. *Absolute alcohol* contains no water, and is of sp. gr. 0·793. The various wines and beers met with in commerce contain different amounts of alcohol, as shown in the following table :

Brandy Gin Whisky	...	From 36 to 60 per cent. by volume.	
Port Sherry	...	About 18 per cent.	„ „
Champagne	...	About 12 per cent.	„ „
Claret Hock	...	From 10 to 12 per cent.	„ „
Beer	...	From 3 to 6 per cent.	„ „

The strength of alcoholic beverages is expressed by the excise as *under* or *over proof*; 25 over proof means that 100 volumes of the spirit will make 125 volumes of proof spirit ; 25 under proof indicates that 100 volumes of the fluid contain 75 volumes of proof spirit.

By the oxidation of alcohol two bodies are obtained, according to the strength of the oxidising agent employed. If the oxidising agent be a weak one, acetic aldehyde (C_2H_4O) is produced. If the oxidising agent be a strong one, acetic acid ($C_2H_4O_2$) is produced. Thus, by distilling ethyl alcohol with manganese dioxide and sulphuric acid, acetic aldehyde is formed, the action of this weak oxidising mixture being merely to abstract two atoms of hydrogen from the alcohol molecule.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{\left\{\begin{matrix}CH_3\\CH_2HO\end{matrix}\right.} + \underset{\text{Oxygen.}}{O} = \underset{\substack{\text{Acetic}\\\text{aldehyde.}}}{\left\{\begin{matrix}CH_3\\COH\end{matrix}\right.} + \underset{\text{Water.}}{H_2O}$$

If the alcohol be distilled with potassium bichromate and sulphuric acid, an atom of oxygen is introduced and acetic acid formed.

$$\underset{\text{Ethyl alcohol.}}{\left\{\begin{array}{l}CH_3\\ CH_2HO\end{array}\right.} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Acetic acid.}}{\left\{\begin{array}{l}CH_3\\ COOH\end{array}\right.} + \underset{\text{Water.}}{H_2O}$$

The metals potassium and sodium act on ethyl alcohol, displacing one atom of hydrogen from the molecule, and forming respectively potassium ethylate (C_2H_5KO) and sodium ethylate (C_2H_5NaO), the latter being sometimes employed as a caustic.

If chlorine gas be passed into rectified spirit, a variety of bodies may be produced :

(i) Aldehyde may be formed by the direct withdrawal of hydrogen by the chlorine.

$$\underset{\text{Ethyl alcohol}}{\left\{\begin{array}{l}CH_3\\ CH_2HO\end{array}\right.} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Acetic aldehyde.}}{\left\{\begin{array}{l}CH_3\\ COH\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{2HCl}$$

(ii) Chloral may be formed by the further action of the chlorine on this aldehyde.

$$\underset{\text{Acetic aldehyde.}}{\left\{\begin{array}{l}CH_3\\ COH\end{array}\right.} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Chloral.}}{\left\{\begin{array}{l}CCl_3\\ COH\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{3HCl}$$

(iii) Ethyl chloride may be formed by the action of the hydrochloric acid, produced in the former reactions, upon some of the undecomposed alcohol.

$$\underset{\text{Ethyl alcohol.}}{C_2H_5HO} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ethyl chloride.}}{C_2H_5Cl} + \underset{\text{Water.}}{H_2O}$$

(iv) Acetic acid may be produced by the oxidation of some of the alcohol by oxygen, this gas being liberated by the action of chlorine on the water contained in the rectified spirit.

$$\underset{\text{Ethyl alcohol.}}{\left\{\begin{array}{l}CH_3\\CH_2HO\end{array}\right.} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Acetic acid.}}{\left\{\begin{array}{l}CH_3\\COOH\end{array}\right.} + \underset{\text{Water.}}{H_2O}$$

(v) Finally, ethyl acetate or acetic ether may be formed by the action of the acetic acid, produced in the former reaction, upon some undecomposed alcohol.

$$\underset{\text{Ethyl alcohol.}}{C_2H_5HO} + \underset{\text{Acetic acid.}}{HC_2H_3O_2} = \underset{\text{Ethyl acetate.}}{C_2H_5C_2H_3O_2} + \underset{\text{Water.}}{H_2O}$$

Ethyl Compounds.

Ethyl chloride (C_2H_5Cl).—This is prepared by the action of phosphorus trichloride on ethyl alcohol.

$$\underset{\text{Ethyl alcohol.}}{3C_2H_5HO} + \underset{\text{Phosphorus trichloride.}}{PCl_3} = \underset{\text{Ethyl chloride.}}{3C_2H_5Cl} + \underset{\text{Phosphorous acid.}}{H_3PO_3}$$

Ethyl iodide (C_2H_5I).—This can be prepared by the action of phosphorus tri-iodide on ethyl alcohol.

$$\underset{\text{Ethyl alcohol.}}{3C_2H_5HO} + \underset{\text{Phosphorus tri-iodide.}}{PI_3} = \underset{\text{Ethyl iodide.}}{3C_2H_5I} + \underset{\text{Phosphorous acid.}}{H_3PO_3}$$

As a rule, the iodide is made by the direct action of phosphorus and iodine on the alcohol : 100 grammes of iodine are added gradually to 50 grammes of alcohol and 10 grammes of amorphous phosphorus, the mixture allowed to stand, and then distilled. The distillate is shaken with dilute potassium hydrate, washed, dried by standing over fused calcium chloride, and finally redistilled ; it is a colourless liquid boiling at 72°.

Ethyl ether ($(C_2H_5)_2O$).—This is commonly known as *ether* or *sulphuric ether*. It is the oxide of ethyl, but the process for its preparation will be rendered more intelligible by regarding it as ethyl alcohol partially dehydrated. Thus, if from two molecules of ethyl alcohol one molecule of water be abstracted, ether is obtained.

$$\underset{\text{Ethyl alcohol.}}{2C_2H_5HO} \quad - \quad \underset{\text{Water.}}{H_2O} \quad = \quad \underset{\text{Ethyl ether.}}{(C_2H_5)_2O}$$

The process for preparing ether on a commercial scale, which is known as the *continuous etherification process*, consists in partially dehydrating ethyl alcohol by means of strong sulphuric acid. This process is carried out by distilling a mixture of sulphuric acid and rectified spirit, the latter being in excess. The ether, as it is formed, distils over, the sulphuric acid remaining in the retort, and therefore, to prevent the sulphuric acid from being in excess, it is necessary that as fast as the ether distils over more alcohol should be run into the retort so that the temperature of the boiling mixture remains between 140° and 145°. If this is effected the process becomes a continuous one; hence its name. The sulphuric acid does not directly withdraw the water from the alcohol, but indirectly, in the two following stages:

(i) The sulphuric acid first forms with the alcohol, hydrogen ethylsulphate (sulphovinic acid or ethylsulphuric acid).

$$\underset{\text{Ethyl alcohol.}}{C_2H_5HO} \quad + \quad \underset{\text{Sulphuric acid.}}{H_2SO_4} \quad = \quad \underset{\text{Hydrogen ethylsulphate.}}{HC_2H_5SO_4} \quad + \quad \underset{\text{Water.}}{H_2O}$$

(ii) This ethylsulphuric acid then reacts with more alcohol, forming ether and sulphuric acid.

$$\underset{\text{Ethyl alcohol.}}{C_2H_5HO} + \underset{\text{Hydrogen ethylsulphate.}}{HC_2H_5SO_4} = \underset{\text{Ether.}}{(C_2H_5)_2O} + \underset{\text{Sulphuric acid.}}{H_2SO_4}$$

It is essential, for the production of ether by this process, that the alcohol should be kept in excess; otherwise, if the sulphuric acid become in excess, it will completely dehydrate the alcohol, forming ethylene or olefiant gas.

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} - \underset{\text{Water}}{H_2O} = \underset{\text{Ethylene.}}{C_2H_4}$$

Properties of ether.—The ether obtained by the process just given contains about 8 per cent. of alcohol, from which it can be purified by agitating with water; on standing, the ether rises to the surface of the water, leaving the alcohol in solution; the ether is then removed from the surface of the water, and distilled with some freshly-made quicklime to free it from the little water that it contains.

Pure ether is a colourless, transparent, very mobile liquid, with a characteristic fragrant smell, and extremely volatile. Its specific gravity is 0·720; it boils at 35°. It is very combustible, producing carbon dioxide and water when burnt. When dropped on the hand it occasions a sharp sensation of cold from its rapid evaporation. Ether is miscible with alcohol in all proportions, but in water it is soluble only to a very small extent. It dissolves many fats, oils, resins and alkaloids.

Ethyl nitrite or **nitrous ether** ($C_2H_5NO_2$), mixed with aldehyde, alcohol and other substances, is contained in Sweet Spirits of Nitre (*Spiritus ætheris nitrosi*, B. P.), which contains 2½ per cent. of ethyl nitrite. This preparation is made by distilling together rectified spirit, copper turnings, sulphuric acid and nitric acid. The copper reduces the nitric acid to nitrous acid.

$$\underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Copper.}}{Cu} = \underset{\text{Nitrous acid.}}{HNO_2} + \underset{\text{Copper oxide.}}{CuO}$$

The nitrous acid then acts upon the alcohol, forming nitrous ether.

$$\underset{\text{Ethyl alcohol.}}{C_2H_5HO} + \underset{\text{Nitrous acid.}}{HNO_2} = \underset{\text{Nitrous ether.}}{C_2H_5NO_2} + \underset{\text{Water.}}{H_2O}$$

The preparation of nitrous ether by this process constitutes a fairly good test for alcohol, the peculiar apple-like odour of nitrous ether being readily recognised.

Ethyl acetate or **acetic ether** ($C_2H_5C_2H_3O_2$).—This is prepared by distilling rectified spirit with sodium acetate and sulphuric acid. The two latter bodies set free acetic acid, which then acts upon the alcohol producing acetic ether.

$$\underset{\text{Ethyl alcohol.}}{C_2H_5HO} + \underset{\text{Acetic acid.}}{HC_2H_3O_2} = \underset{\text{Ethyl acetate.}}{C_2H_5C_2H_3O_2} + \underset{\text{Water.}}{H_2O}$$

Acetic ether is a colourless liquid boiling at 77° ; it has an agreeable fruity odour. Its formation by heating sulphuric acid with alcohol and an acetate is often used as a test for an acetate.

Hydrogen ethyl sulphate or **sulphovinic acid** ($HC_2H_5SO_4$) is prepared by warming a mixture of equal parts of ethyl alcohol and sulphuric acid.

$$\underset{\text{Ethyl alcohol.}}{C_2H_5HO} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sulphethylic acid.}}{HC_2H_5SO_4} + \underset{\text{Water.}}{H_2O}$$

It can also be prepared by heating ethylene with strong sulphuric acid.

It is a thick sour liquid; when boiled with water it yields alcohol, heated with alcohol it gives ether, heated alone it yields ethylene.

Ethyl hydrosulphide or **ethyl-mercaptan** (C_2H_5HS).—This is prepared by distilling a mixture of potassium hydrosulphide and calcium ethyl sulphate.

$$\underset{\substack{\text{Calcium}\\\text{ethylsulphate.}}}{Ca(C_2H_5SO_4)_2} + \underset{\substack{\text{Potassium}\\\text{hydrosulphide.}}}{2KHS} = \underset{\substack{\text{Ethyl}\\\text{mercaptan.}}}{2C_2H_5HS} + \underset{\substack{\text{Calcium}\\\text{sulphate.}}}{CaSO_4} + \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4}$$

It is a liquid with an extremely unpleasant nauseating odour.

Acetic aldehyde or **ordinary aldehyde** $\left(\left\{\begin{matrix}CH_3\\COH\end{matrix}\right.\right)$.—It may be prepared—

(i) By the oxidation of ethyl alcohol by means of manganese dioxide and sulphuric acid.

$$\underset{\substack{\text{Manganese}\\\text{dioxide.}}}{2MnO_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Manganous}\\\text{sulphate.}}}{2MnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{O_2}$$

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{2\left\{\begin{matrix}CH_3\\CH_2HO\end{matrix}\right.} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Aldehyde.}}{2\left\{\begin{matrix}CH_3\\COH\end{matrix}\right.} + \underset{\text{Water}}{2H_2O}$$

(ii) By the action of chlorine upon a mixture of ethyl alcohol and water, the chlorine uniting with the

COH | C-O-H |

hydrogen of the water, the oxygen of which oxidises the alcohol to aldehyde.

$$\underset{\text{Ethyl alcohol.}}{2C_2H_6O} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Aldehyde.}}{2C_2H_4O} + \underset{\text{Water.}}{2H_2O}$$

Properties.—Aldehyde is a colourless liquid with a peculiar smell, boils at 20·8°, and is very inflammable. Its name is derived from an abbreviation of the expression *alcohol dehydrogenated*, as it is alcohol deprived of part of its hydrogen. By exposure to the air it absorbs oxygen and becomes converted into acetic acid; reducing agents convert it into alcohol. Chlorine acts upon it, forming chloral (*see* below). A polymeric modification of it, viz. *paraldehyde* ($C_6H_{12}O_3$), is prepared by adding a few drops of concentrated sulphuric acid to aldehyde, when the liquid becomes hot, and, on cooling, crystals of paraldehyde form. When warmed with potassium hydrate aldehyde is converted into a solid brown mass (*aldehyde resin*). Aldehyde is a powerful reducing substance precipitating silver in the metallic state from ammoniacal solution of silver nitrate. It combines with free ammonia to form colourless crystals of *aldehyde ammonia* (CH_3, COH, NH_3), which are decomposed by acids, liberating aldehyde.

Trichloraldehyde or **chloral** $\left(\left\{\begin{matrix}CCl_3\\COH\end{matrix}\right.\right)$.— This body constitutes what is commonly known as chloral, the hydrate of which is *chloral hydrate*, a substance largely used in medicine as a hypnotic. Chloral is prepared by the prolonged action of chlorine upon absolute alcohol. The reaction may, for the sake of simplicity, be regarded as taking place in the two following stages:

(i) Chlorine first converts the alcohol into aldehyde.

$$\begin{array}{ccccccc} \left\{\begin{matrix}CH_3\\CH_2HO\end{matrix}\right. & + & Cl_2 & = & \left\{\begin{matrix}CH_3\\COH\end{matrix}\right. & + & 2HCl \\ \text{Ethyl alcohol.} & & \text{Chlorine.} & & \text{Aldehyde.} & & \text{Hydrochloric acid.} \end{array}$$

(ii) The chlorine then acts upon the aldehyde, abstracting three-fourths of the hydrogen, replacing it by chlorine, and so producing chloral.

$$\begin{array}{ccccccc} \left\{\begin{matrix}CH_3\\COH\end{matrix}\right. & + & 3Cl_2 & = & \left\{\begin{matrix}CCl_3\\COH\end{matrix}\right. & + & 3HCl \\ \text{Aldehyde.} & & \text{Chlorine.} & & \text{Chloral.} & & \text{Hydrochloric acid.} \end{array}$$

Properties.—Chloral is a heavy liquid, with an extremely pungent, irritating odour. It is converted by the action of alkalies into chloroform and a formate of the alkali metal. Thus, with caustic potash it yields chloroform and potassium formate.

$$\begin{array}{ccccccc} C_2HCl_3O & + & KHO & = & CHCl_3 & + & KCHO_2 \\ \text{Chloral.} & & \text{Caustic potash} & & \text{Chloroform.} & & \text{Potassium formate.} \end{array}$$

With slaked lime it yields chloroform and calcium formate.

$$\begin{array}{ccccccc} 2C_2HCl_3O & + & Ca(HO)_2 & = & 2CHCl_3 & + & Ca(CHO_2)_2 \\ \text{Chloral.} & & \text{Slaked lime.} & & \text{Chloroform.} & & \text{Calcium formate.} \end{array}$$

Just as aldehyde is oxidised by nitric acid to acetic acid, so chloral or trichloraldehyde is oxidised by nitric acid to trichloracetic acid, thus:

$$\begin{array}{ccccc} 2\left\{\begin{matrix}CH_3\\COH\end{matrix}\right. & + & O_2 & = & 2\left\{\begin{matrix}CH_3\\COOH\end{matrix}\right. \\ \text{Aldehyde.} & & \text{Oxygen.} & & \text{Acetic acid.} \end{array}$$

$$2\left\{\begin{array}{l}CCl_3\\COH\end{array}\right. + O_2 = 2\left\{\begin{array}{l}CCl_3\\COOH\end{array}\right.$$

Chloral. Oxygen. Trichloracetic acid.

Chloral, when mixed with water, produces a crystalline mass of *chloral hydrate.*

Chloral hydrate $\left(C_2HCl_3O, H_2O, \text{ or } \left\{\begin{array}{l}CCl_3\\C(HO)_2H\end{array}\right.\right)$. —This body, as previously mentioned, is prepared by the action of water on chloral. It is a white crystalline solid, with a very faint odour of the liquid chloral attached to it. It is largely used in medicine as a hypnotic, and has been stated to be decomposed by the sodium carbonate of the blood into chloroform, though it is very doubtful whether such a decomposition takes place.

Chloral hydrate is decomposed by contact with caustic alkalies into chloroform and formate of the alkali metal. Chloral hydrate is therefore incompatible with alkalies, and should never be prescribed with them in medicine.

Chloroform ($CHCl_3$).—This body is actually a derivative of methane (CH_4), from which it may be obtained by the action of chlorine (*see* page 388); but since all the chloroform of commerce is prepared by the decomposition of chloral, it is more convenient to describe its preparation in the present section. Chloroform, on the commercial scale, is prepared by distilling a mixture of rectified spirit, chlorinated lime (bleaching powder), and slaked lime. The formation of chloroform takes place in the three following stages:

(i) Some of the oxygen of the chlorinated lime ($CaCl_2$, $CaCl_2O_2$) oxidises the alcohol to aldehyde.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{\left\{\begin{array}{l}CH_3\\CH_2HO\end{array}\right.} + \underset{\text{Oxygen.}}{O} = \underset{\text{Aldehyde.}}{\left\{\begin{array}{l}CH_3\\COH\end{array}\right.} + \underset{\text{Water.}}{H_2O}$$

(ii) The aldehyde is then converted, by some of the chlorine of the chlorinated lime, into chloral.

$$\underset{\text{Aldehyde.}}{\left\{\begin{array}{l}CH_3\\COH\end{array}\right.} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Chloral.}}{\left\{\begin{array}{l}CCl_3\\COH\end{array}\right.} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{3HCl}$$

(iii) The chloral is then decomposed by the slaked lime into chloroform and calcium formate, the chloroform distilling over.

$$\underset{\text{Chloral.}}{2C_2HCl_3O} + \underset{\substack{\text{Slaked}\\\text{lime.}}}{Ca(HO)_2} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\substack{\text{Calcium}\\\text{formate.}}}{Ca(CHO_2)_2}$$

Properties of chloroform.—The sp. gr. of chloroform is 1·5. The medicinal chloroform contains a minute amount of alcohol, and is of sp. gr. 1·497; it boils at 61°. It is a thin colourless liquid, with a sweetish taste and a pleasant characteristic odour. It is readily soluble in alcohol and ether, and slightly so in water (*Aqua chloroformi*). It is difficult to kindle and burns with a greenish smoky flame.

Iodoform (CHI_3).—This body is analogous in constitution to chloroform. It is prepared by warming together sodium carbonate, alcohol, water, and iodine. The production of iodoform constitutes a very delicate test for alcohol. Iodoform occurs in yellow, shiny scales, almost insoluble in water, but soluble in alcohol and ether. It has a characteristic penetrating and somewhat unpleasant smell.

Butyl chloral $\left(C_4H_5Cl_3O, \text{ or } \left\{\begin{array}{l}C_3H_4.Cl_3\\COH\end{array}\right.\right)$.—A hydrate of this body is used in medicine under the name of *croton chloral*, which was the original name erroneously applied to it. It is a body corresponding in its constitution to ordinary chloral, since it is trichlor-butyl-aldehyde, that is, it is butyl aldehyde (C_4H_8O), from the molecule of which three atoms of hydrogen have been displaced by three atoms of chlorine. It is a product of the action of dry chlorine on ordinary aldehyde in the cold. Its hydrate ($C_4H_5Cl_3O$, H_2O) (*Butyl chloral hydras*) is the ordinary *croton chloral* used in medicine.

AMYL ALCOHOL.

Amyl alcohol ($C_5H_{11}HO$).—Eight isomerides of this body (which derives its name from *amylum*—starch) can theoretically exist. Two of these are found in the *fusel oil* obtained in the preparation of ordinary alcohol from the different forms of starch. They are also contained in crude or raw whisky, but the sugar obtained from potato starch yields a more considerable amount, and hence this alcohol is sometimes called *potato oil.*

Properties.—Commercial amyl alcohol is an oily colourless liquid having a peculiar unpleasant odour. It is not appreciably soluble in water, but floats on the surface of it like an oil; hence its name *fusel oil.* When oxidised it yields *valerianic acid.*

Amyl nitrite ($C_5H_{11}NO_2$).—This compound is prepared by a process similar to that employed in the preparation of ethyl nitrite, namely, by distilling a mixture of amyl alcohol, copper turnings, sulphuric and nitric acids.

Amyl acetate ($C_5H_{11}C_2H_3O_2$).—This substance is prepared by distilling amyl alcohol with sodium acetate and sulphuric acid. It constitutes the *jargonelle pear essence.*

Ethylene [illegible] glycol

$_2H_4(OH)_2$

2. DIHYDRIC ALCOHOLS.

These are hydrates of the bivalent hydrocarbon radicles, and therefore contain two groups of hydroxyl in the molecule. Several of them exist under the name of *glycols*, so named from their sweet taste, but as they are of no importance in medicine, a brief description of one of them only will be given here.

Ethylene glycol ($C_2H_4(HO)_2$).—This is prepared by acting on ethylene with bromine to form ethylene dibromide ($C_2H_4Br_2$), and then decomposing with moist silver oxide.

$$\underset{\text{Ethylene dibromide.}}{C_2H_4Br_2} + \underset{\text{Silver oxide.}}{Ag_2O} + \underset{\text{Water.}}{H_2O} = \underset{\text{Glycol.}}{C_2H_4(HO)_2} + \underset{\text{Silver bromide.}}{2AgBr}$$

$_3H_5(OH)_3$ Glyc[illegible]

3. TRIHYDRIC ALCOHOLS.

These are the hydrates of the trivalent hydrocarbon radicles, and therefore contain in the molecule three hydroxyl groups. Only one of them is employed in medicine, viz. *glycerin.*

Glycerin or glyceryl hydrate ($C_3H_5(HO)_3$).—Most fats and oils are compounds of the trivalent radicle glyceryl (C_3H_5) with the higher fatty acids. When these fats and oils are saponified by boiling with caustic soda, the radicle glyceryl, displaced by the sodium, combines with three hydroxyl groups to form glycerin ($C_3H_5(HO)_3$), whilst the sodium combines with the radicle of the fatty acid to form a soap, thus :

$$\underset{\text{Glyceryl oleate.}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\text{Sodium hydrate.}}{3NaHO} = \underset{\text{Sodium oleate.}}{3NaC_{18}H_{33}O_2} + \underset{\text{Glycerin.}}{C_3H_5(HO)_3}$$

H_5 OH = glycerin C_3H_5 O(NO₂) = nitro-
OH O(NO₂) Glycerin
formed by [illegible]
H atom with (NO

Glycerin is more conveniently prepared by decomposing melted suet (glyceryl stearate) by means of superheated steam, when the glycerin and stearic acid are carried over in the current of steam, the stearic acid setting to a solid, and the glycerin, diluted with the condensed steam, being obtained as a liquid.

$$\underset{\text{Glyceryl stearate.}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Stearic acid.}}{3HC_{18}H_{35}O_2} + \underset{\text{Glycerin.}}{C_3H_5(HO)_3}$$

Properties of glycerin.—Glycerin is a colourless and very viscid liquid of sp. gr. 1·27. It has a very sweet taste and mixes with water in all proportions. When heated by itself or with bisulphate of potash ($HKSO_4$) it decomposes, losing the elements of water and yielding a substance *acrolein* (C_3H_4O), which has an intensely pungent odour.

Glycerin treated with a mixture of strong nitric and sulphuric acids, forms *nitro-glycerin* ($C_3H_5(NO_3)_3$), a heavy oily liquid, which produces by percussion a terrible explosion; in its liquid form it is very dangerous to handle, and is, therefore, for blasting and other purposes, made into *dynamite*, which consists of porous silica, in the form of infusorial earth, saturated with nitro-glycerin. Ordinary dynamite usually consists of 75 parts of nitro-glycerin and 25 parts of silica. Tablets of chocolate containing $\frac{1}{100}$th of a grain of nitro-glycerin are used in medicine (*Tabellæ Trinitrini*).

When oxidised with ordinary nitric acid glycerin yields glyceric acid, a non-explosive substance

$$\left\{\begin{array}{l} CH_2HO \\ CHHO. \\ COOH \end{array}\right.$$

CHAPTER VII.

POLYHYDRIC ALCOHOLS—CARBOHYDRATES.

Mannite—Starch—Glycogen—Dextrin—Cellulose—Cane Sugar—Milk Sugar—Maltose—Glucose—Lævulose—Galactose.

The polyhydric alcohols have become, of late years, of great theoretical importance, in consequence of their close connection with glucose, lævulose, and other sugars. The most interesting in this connection is

Mannite or Mannitol $\left(\left\{\begin{array}{l} CH_2HO \\ (CHHO)_4 \\ CH_2HO \end{array}\right. \text{ or } C_6H_8(HO)_6,\right)$,

a hexhydric alcohol found in manna, the dried sap of a species of ash; it is colourless, crystalline and very sweet; it can be formed artificially by reducing grape sugar with sodium amalgam.

The Carbohydrates.

These substances owe their name to the old idea that they were hydrates of carbon; they are really various compounds of carbon, hydrogen, and oxygen, in which the atoms of hydrogen are twice as numerous as the atoms of oxygen. They can be conveniently divided into three chief groups—

I.—The amyloses or polysaccharoses—
Starch; Dextrin; Cellulose; having the formula $(C_6H_{10}O_5)_n$.

II.—The disaccharoses—
Cane sugar; Milk sugar; Maltose; having the formula $C_{12}H_{22}O_{11}$.

III.—The glucoses or monoses—
Glucose, dextrose or grape sugar; Lævulose or fruit sugar; Galactose; having the formula $C_6H_{12}O_6$.

$H_{10}O_5$ Amyloses

Starch ($C_6H_{10}O_5$).—Starch is contained in certain roots, seeds, soft stems, potatoes, and various grains, such as wheat, maize, etc. Arrowroot and rice contain considerable quantities of starch. Starch is prepared from roots or seeds by crushing them and placing them upon a sieve or strainer, through which water is flowing. The water mechanically carries the starch through the sieve, leaving fibrous and cellular substances behind. The water is then allowed to stand, and the starch deposits as a white sediment, from which the water is poured off, and which is finally dried. Starch may be prepared from wheat and other flours by placing the flour in a muslin or calico bag and wringing it out several times with water, when the starch is mechanically carried away by the water, a sticky substance, gluten, being left in the bag.

Properties of starch.—The different starches are white powders, which, when examined under the microscope, are seen to consist of granules, the granules of the various starches differing in size and shape. Starch is insoluble in cold water, the granules being unaffected by it, but in hot water the granules break up, being in part dissolved and in part remaining in suspension, forming what is called "decoction or mucilage of starch." Starch, as employed for laundry purposes, is coloured a light-blue with indigo, which is introduced in order to neutralise the faint yellow colour of recently-washed linen. If a solution of free iodine is added to a cold decoction of starch, a dark-blue colour, due to a molecular compound of iodine and starch, is developed. If heat be applied to the blue liquid, the blue colour disappears, owing to the dissociation of the starch and iodine by the heat. If the heat be quickly withdrawn, the blue colour reappears on cooling. A solution of starch does not reduce an alkaline copper solution when boiled with it. If starch is boiled with dilute sulphuric acid, it is first converted into dextrin and then, by assimilation of water, into grape sugar. Starch is also converted into grape sugar under the influence of certain ferments, such as ptyalin in saliva, the pancreatic ferments in pancreatic juice, etc. Diastase, the ferment in barley, converts starch into a mixture of dextrin and maltose.

$$\underset{\text{Starch.}}{3C_6H_{10}O_5} + \underset{\text{Water.}}{H_2O} = \underset{\text{Dextrin.}}{C_6H_{10}O_5} + \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}}$$

This is the first step in brewing.

Test for starch.—The blue colour produced by a solution of free iodine constitutes an extremely delicate test for starch.

Glycogen ($C_6H_{10}O_5$).—This substance, which is an isomer of starch, is found in the livers of man and animals. It is prepared by finely chopping up fresh liver and boiling it with water, which dissolves out the glycogen; from this solution it is precipitated by the addition of alcohol.

Properties of glycogen.—Glycogen is a white powder, soluble in water, in which it forms an opalescent solution. A solution of free iodine gives a mahogany-brown colour to a solution of glycogen; it is readily converted into grape sugar by contact with certain ferments.

Dextrin ($C_6H_{10}O_5$).—This substance is prepared from starch either by baking it in an oven, or by boiling it with dilute sulphuric acid, or by the action of ferments such as yeast and diastase upon it. The

$O(NO_2)$

first-mentioned method is the best, as by the other methods the dextrin is quickly converted into grape sugar.

Properties of dextrin.—Dextrin is a whitish powder, readily soluble in cold water, in which it forms a sticky or mucilaginous solution. It is commonly employed under the name of *British gum.* Commercial dextrin gives with a solution of free iodine a mahogany-brown colour, which disappears on the application of heat, and does not reappear on cooling, thus distinguishing it from glycogen.

Cellulose $(C_6H_{10}O_5)_n$.—This substance is also called ~~*lignin.* It is obtained~~ in its purest form as linen, cotton, cotton-wool, Swedish filter-paper, etc. Cellulose is insoluble in both cold and boiling water.

When treated with solution of caustic soda cellulose undergoes a marked change, shrinking, etc.; this treatment is known as *mercerisation.* Mercerised cotton is largely used at the present day as a substitute for silk. When treated with nitric acid cellulose forms nitrates; the two which are most important are—

Pyroxylin or *di-nitrocellulose* $(C_6H_8(NO_3)_2O_3)$.—This is prepared by steeping cellulose in a mixture of sulphuric and nitric acids, the strong sulphuric acid being employed to absorb the water produced by the action of the nitric acid on the cellulose.

$$\underset{\text{Cellulose.}}{C_6H_{10}O_5} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Pyroxylin.}}{C_6H_8(NO_3)_2O_3} + \underset{\text{Water.}}{2H_2O}$$

This substance, dissolved in a mixture of alcohol and ether, constitutes *collodion*, which is employed for producing a covering or artificial skin to abrasions, etc., of the skin.

Gun-cotton, or *tri-nitrocellulose* $(C_6H_7(NO_3)_3O_2)$.—This substance is prepared by steeping cellulose in the strongest sulphuric and nitric acids.

$$\underset{\text{Cellulose.}}{C_6H_{10}O_5} + \underset{\text{Nitric acid.}}{3HNO_3} = \underset{\text{Gun-cotton.}}{C_6H_7(NO_3)_3O_2} + \underset{\text{Water.}}{3H_2O}$$

This is the ordinary gun-cotton employed for blasting purposes and in gun-cotton cartridges. It is an explosive, in that it contains sufficient oxygen for the combustion of the carbon and hydrogen contained in it. It produces, when exploded, large volumes of the two oxides of carbon, steam, and nitrogen which are, in addition, greatly expanded by the heat produced by the chemical decomposition. It is the sudden production and violent expansion of these gases that cause the destruction produced by gun-cotton when exploded with a detonator; it is a curious fact that if gun-cotton be lighted with a match it burns away rapidly without exploding. It requires a detonation to develop its destructive force.

If a piece of white filter paper be dipped in a cold mixture of 2 volumes of strong sulphuric acid with 1 volume of water for a few minutes, and then thoroughly washed, it is converted into a substance like parchment, and is known as *parchment paper*, largely used for wrapping and for diffusion experiments.

Cellulose gradually dissolves in strong sulphuric acid, and the solution, when diluted and boiled, is found to contain dextrin and grape sugar.

Cane sugar, sucrose, or saccharose ($C_{12}H_{22}O_{11}$).—This sugar exists in the sugar cane, date, beetroot, and in the sap of the sugar maple. It is extracted from the sugar cane by crushing the canes in order to squeeze out the juice, to which is then added some slaked lime; the mixture is boiled, and the mechanical impurities are allowed to settle; the liquor, poured off from these impurities, is concentrated by evaporation and set aside to cool, when crystals of *raw or brown sugar* settle out, the viscid mother liquid constituting *molasses*. To obtain the *white or loaf sugar*, the brown sugar is dissolved in water, and some serum of blood and a little slaked lime are added; the liquid is heated, and allowed to stand, when the coagulum produced from the serum of blood settles down, carrying with it impurities. The solution is filtered through animal charcoal to decolorise it, and is evaporated to a syrup, which is poured into conical moulds, within which, on cooling, the white or loaf sugar crystallises. In all modern works the sugar syrup is evaporated in large copper boilers, from which the air has been partially removed, known as *vacuum pans*. In these pans the syrup boils at 65·5°, its boiling point being lowered by the vacuum about 45°.

Properties of cane sugar.—Cane sugar is readily soluble in both cold and hot water; its solution does not reduce an alkaline copper solution. Nitric acid first converts it into saccharic acid ($C_6H_{10}O_8$), and then into oxalic acid. It combines with alkalies and with lime to form soluble saccharates. If boiled with dilute sulphuric acid, water is assimilated, and grape sugar is formed, or rather invert sugar, which is a mixture of dextrose and lævulose.

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + \underset{\text{Water.}}{H_2O} = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Lævulose.}}{C_6H_{12}O_6}$$

Cane sugar does not ferment directly, but there is a ferment present in ordinary yeast, which converts it into invert sugar, and then the yeast decomposes the latter into alcohol and carbon dioxide. If solid cane sugar is carefully heated, a reddish-brown liquid is obtained, which is *burnt sugar* or *caramel.*

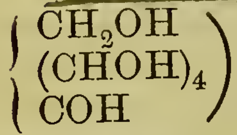
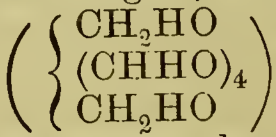
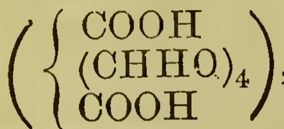
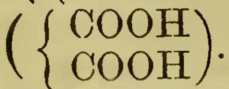
Tests for cane sugar.—Cane sugar is easily charred by strong sulphuric acid; it gives a red colour and then a brown precipitate when boiled with strong hydrochloric acid; it does not reduce an alkaline copper solution.

Milk sugar or lactose ($C_{12}H_{22}O_{11},H_2O$).—This sugar is contained in milk, from which it may be prepared by precipitating the curds by the addition of rennet or some acid, filtering, and evaporating the clear whey to a low bulk, when the milk sugar crystallises out on cooling.

Properties of milk sugar.—It is less soluble in water than any of the other sugars, and also less sweet. It does not undergo fermentation in contact with yeast, or only after a very long time; in contact with the ferment *penicillium glaucum* it undergoes lactic acid fermentation; it is this conversion of milk sugar into lactic acid which is the cause of the souring of milk when exposed to the air, the spores of penicillium glaucum being always present in the air, and settling on the exposed surface of the milk. When boiled with dilute acids, lactose is converted into a mixture of galactose and dextrose. Strong nitric acid oxidises lactose into mucic and saccharic acids.

Tests for milk sugar.—A solution of milk sugar reduces Fehling's solution when boiled with it, and in this respect it resembles glucose. It can be distinguished from glucose, in the solid state, by its being so much less soluble in water, and in solution by not undergoing fermentation in contact with yeast; whereas a solution of glucose readily ferments in contact with yeast when the mixture is left in a warm place.

Maltose ($C_{12}H_{22}O_{11},H_2O$).—This sugar is obtained by the action of diastase on starch, and gives to malt its sweet taste; it crystallises in needles which are readily soluble in water. It ferments readily with yeast. Boiled with dilute sulphuric acid it is completely converted into glucose. It reduces an alkaline solution of copper, but only to two-thirds the extent of an equal weight of glucose.

Glucose, dextrose, grape sugar ($C_6H_{12}O_6$, or  $\left\{\begin{array}{l} CH_2OH \\ (CHOH)_4 \\ COH \end{array}\right)$.—This sugar occurs in grapes, honey, and diabetic urine; it can be extracted from any of these sources, and it can be prepared by heating cane sugar with dilute sulphuric acid, when it is obtained mixed with lævulose, or by boiling maltose or starch with dilute acid. It is less sweet, less soluble in water and more difficult to crystallise than cane sugar, it ferments readily with yeast, forming alcohol, carbon dioxide, and traces of other substances. Its constitutional formula is known, and it has been prepared artificially from formaldehyde and from glycerin. It is obvious from its formula that it is an aldehyde, as it contains the characteristic group COH; it is therefore a reducing substance and when reduced by sodium amalgam, it yields the corresponding alcohol  $\left(\left\{\begin{array}{l} CH_2HO \\ (CHHO)_4 \\ CH_2HO \end{array}\right.\right)$ mannite; just as acetic aldehyde yields on reduction ethyl alcohol. Nitric acid converts it first into saccharic acid  $\left(\left\{\begin{array}{l} COOH \\ (CHHO)_4 \\ COOH \end{array}\right.\right)$, and ultimately into oxalic acid  $\left(\left\{\begin{array}{l} COOH \\ COOH \end{array}\right.\right)$.

Tests for glucose.—Glucose does not blacken when mixed in the cold with strong sulphuric acid. It reduces an alkaline solution of copper. This reduction test can be applied in two forms: (1) *Trommer's* test; to a small quantity of 5 per cent. solution of copper sulphate add grape sugar and then caustic potash drop by drop until a clear dark blue solution is obtained; on heating this solution the blue colour disappears and a precipitate, first yellow and then red, is obtained. The cupric salt is reduced by the glucose to yellow cuprous hydrate, which is ultimately converted into red cuprous oxide. (2) *Fehling's* test. This consists of two solutions, one containing 34·6 grammes of crystallised copper sulphate in 500 c.c. of water; the other, 173 grammes of Rochelle salt and 60 grammes of caustic soda in 500 c.c. These solutions are mixed in equal volumes and the grape sugar added, when, on heating, a decomposition similar to that described in the Trommer's test takes place. Ten cubic centimetres of the mixed solutions are reduced by ·05 gramme of glucose.

Lævulose or **fruit sugar** $\left(C_6H_{12}O_6 \text{ or } \left\{\begin{array}{l} CH_2OH \\ (CHOH)_3 \\ CO(CH_2OH) \end{array}\right.\right).$

—This is an isomer of ordinary grape sugar or dextrose, it is a ketone. It occurs in small quantities in honey, and in many fruits mixed with dextrose. It is distinguished from dextrose by its solution turning a ray of polarised light to the left, whereas a solution of dextrose turns it always to the right. It is best prepared by the inversion of cane sugar, which consists in boiling the cane sugar with dilute sulphuric acid, when a mixture of dextrose and lævulose is obtained.

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + \underset{\text{Water.}}{H_2O} = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Lævulose.}}{C_6H_{12}O_6}$$

To separate the two sugars advantage is taken of the fact that they both form compounds with lime, the dextrose-lime compound being soluble, while the lævulose-lime compound is insoluble. To the solution of the two sugars slaked lime is therefore added, and the mixture filtered; on passing carbon dioxide through the filtrate, the lime is precipitated as calcium carbonate, and the glucose is left in solution. If the insoluble lævulose-lime compound is suspended in water and carbon dioxide passed through, calcium carbonate is precipitated, and the lævulose, in a pure state, is left in solution.

Tests for lævulose. — Lævulose reduces Fehling's solution in a similar manner to dextrose, but is distinguished from dextrose, as previously mentioned, by its action on polarised light.

Action of solutions of sugar on polarised light.—When a ray of polarised light passes through a solution of a sugar, it is twisted to the right or the left according to the nature of the sugar, and to a greater or less extent according to the strength and depth of the solution through which the ray passes. Thus, solutions of cane sugar, milk sugar, maltose, and dextrose or glucose twist the ray of polarised light in the direction in which the hands of a watch rotate—*i.e.* to the right, and are called *dextrorotatory substances.* Lævulose or fruit sugar twists the ray to the left, and is called a *lævorotatory substance.*

Constitution of the sugars.—Much light has been thrown on the constitution of the sugars during the last few years by the researches of Emil Fischer. Thus, we now know that grape sugar is an aldehyde containing the group COH, whilst lævulose is a ketone having the group $CO(CH_2OH)$. Fischer has also prepared some twenty new sugars. Much of this advance is due to the discovery that the various sugars form characteristic crystalline products with phenylhydrazine $\left(\left\{\begin{matrix}NH_2\\NHC_6H_5\end{matrix}\right.\right)$ (a body prepared from anilin by the action of sodium nitrite, and subsequent reduction by stannous chloride), which are more or less insoluble, and can be identified by their crystalline form and melting-point, so that the various sugars can be thus isolated and purified. For instance, glucose can be separated from urine by warming 50 c.c. with

1 gramme of phenylhydrazine hydrochloride and 2 grammes of sodium acetate. On allowing the mixture to cool, characteristic yellow needles will separate. These crystals consist of a complicated compound called an *osazone*—in this case glucosazone ($C_6H_{10}O_4(N.NHC_6H_5)_2$). Similarly, maltose forms maltosazone, etc.

$_4$ | CH_2OH | COH | $CO{-}OH.$ | CH_3|$_2$

$_6$ | $\begin{matrix}CH_3\\CH_2OH\end{matrix}$ | $\begin{matrix}CH_3\\COH.\end{matrix}$ | $\begin{matrix}CH_3\\CO{-}OH.\end{matrix}$ | $(C_2H_5$

CHAPTER VIII.

ORGANIC ACIDS.

1. Monobasic Organic Acids—The Fatty Acids—Formic Acid—Acetic Acid—Butyric Acid—Palmitic and Stearic Acids—Fats and Soaps—Lactic Acid—2. Dibasic Organic Acids—Oxalic Acid—Succinic Acid—Malic Acid—Tartaric Acid—3. Tribasic Organic Acids—Citric Acid.

ALL organic acids contain at least one monovalent group of the radicle carboxyl or oxatyl (COOH). The simplest organic acids are formic acid, in which oxatyl is united to hydrogen $\left\{\begin{matrix}H\\COOH\end{matrix}\right.$ and oxalic acid, which contains only two oxatyl groups $\left(\left\{\begin{matrix}COOH\\COOH\end{matrix}\right.\right)$.

The basicity of an organic acid depends upon the number of oxatyl groups which is contained in the molecule; thus, formic acid is monobasic, oxalic acid dibasic, etc. There are several homologous series of organic acids, but the most important is the *fatty series*, so called because the higher members of the series are found as salts of glyceryl in fats. Many of these fatty acids are found in nature; thus, formic acid occurs in ants, butyric acid in rancid butter, etc.

The fatty acids.—These acids form a homologous series, all having the general formula $\left\{\begin{matrix}C_nH_{2n+1}\\COOH\end{matrix}\right.$. The first nine acids are colourless liquids, showing an average rise of about 22° in their boiling-points for each addition of CH_2; thus, butyric acid $\left(\left\{\begin{matrix}C_3H_7\\COOH\end{matrix}\right.\right)$ boils at 163·2°, valeric acid $\left(\left\{\begin{matrix}C_4H_9\\COOH\end{matrix}\right.\right)$ at 184·5°. The acid $\left\{\begin{matrix}C_9H_{19}\\ COOH\end{matrix}\right.$ and higher members are solids. These acids can be obtained (1) by oxidation of the corresponding alcohols or aldehydes with sulphuric acid and potassium bichromate—

$$\underset{\text{Ethyl alcohol.}}{\left\{\begin{matrix}CH_3\\ CH_2HO\end{matrix}\right.} + \underset{\text{Oxygen.}}{2O} = \underset{\text{Acetic acid.}}{\left\{\begin{matrix}CH_3\\ COOH\end{matrix}\right.} + \underset{\text{Water;}}{H_2O}$$

(2) by the action of bases or acids upon the cyanides of the alcohol radicles—

$$\underset{\substack{\text{Ethyl}\\ \text{cyanide.}}}{\left\{\begin{matrix}C_2H_5\\ CN\end{matrix}\right.} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{HCl} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Propionic}\\ \text{acid.}}}{\left\{\begin{matrix}C_2H_5\\ COOH\end{matrix}\right.} + \underset{\substack{\text{Ammonium}\\ \text{chloride;}}}{NH_4Cl}$$

(3), by fermentation and destructive distillation of wood, etc.

General reactions.—(1) When heated for some time with the alcohols, the acid combines with the alcohol to form an *ester*.

$$\underset{\text{Ethyl alcohol.}}{C_2H_5HO} + \underset{\text{Acetic acid.}}{HC_2H_3O_2} = \underset{\text{Ethyl acetate.}}{C_2H_5C_2H_3O_2} + \underset{\text{Water.}}{H_2O}$$

The bouquet in old wine is believed to be developed in this way owing to the slow formation of the fragrant esters.

(2) When heated with chlorine (or bromine) a chloracid is formed.

$$\underset{\substack{\text{Acetic}\\ \text{acid.}}}{\left\{\begin{matrix}CH_3\\ COOH\end{matrix}\right.} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Chloracetic}\\ \text{acid.}}}{\left\{\begin{matrix}CH_2Cl\\ COOH\end{matrix}\right.} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{HCl}$$

These chloracids undergo two very important decompositions :—

(*a*) Heated with a solution of ammonia in alcohol, the chlorine is replaced by the amido group, NH_2, and an *amido acid* formed.

$$\begin{array}{ccccccc} \left\{\begin{matrix}CH_2Cl\\COOH\end{matrix}\right. & + & 2NH_3 & = & \left\{\begin{matrix}CH_2NH_2\\COOH\end{matrix}\right. & + & NH_4Cl \\ \text{Chloracetic acid.} & & \text{Ammonia.} & & \text{Amidoacetic acid or glycocol.} & & \text{Ammonium chloride.} \end{array}$$

(*b*) When treated with silver hydrate, the chlorine is replaced by hydroxyl, and a *hydroxyacid* is formed.

$$\begin{array}{ccccccccc} 2\left\{\begin{matrix}CH_2Cl\\COOH\end{matrix}\right. & + & Ag_2O & + & H_2O & = & 2\left\{\begin{matrix}CH_2HO\\COOH\end{matrix}\right. & + & 2AgCl \\ \text{Chloracetic acid.} & & \text{Silver oxide.} & & \text{Water.} & & \text{Hydroxyacetic or glycollic acid.} & & \text{Silver chloride.} \end{array}$$

(3) If, instead of chlorine, we use phosphorus trichloride, the chlorine replaces the HO in the oxatyl group, the acid character of the body is lost, and we have the chloride of the acid radicle acetyl formed.

$$\begin{array}{ccccccc} 3\left\{\begin{matrix}CH_3\\COOH\end{matrix}\right. & + & PCl_3 & = & 3\left\{\begin{matrix}CH_3\\COCl\end{matrix}\right. & + & H_3PO_3 \\ \text{Acetic acid.} & & \text{Phosphorous chloride.} & & \text{Acetyl chloride.} & & \text{Phosphorus acid.} \end{array}$$

Acetic acid may be regarded as the hydrate or hydroxide of acetyl $(C_2H_3O)HO$.

1. MONOBASIC ORGANIC ACIDS.

Formic acid $\left(HCHO_2, \text{ or } \left\{\begin{matrix}H\\COOH\end{matrix}\right.\right)$.—This acid occurs in nature in red ants and in stinging nettles. It can be prepared by the oxidation of methyl alcohol, either by dropping it on to spongy platinum, the occluded oxygen of which oxidises it to formic acid; or by distilling methyl alcohol with potassium bichromate and sulphuric acid, which in presence of the alcohol evolve oxygen, with formation of potassium and chromium sulphates.

$$\underset{\text{Methyl alcohol.}}{\left\{\begin{matrix}\mathrm{H}\\\mathrm{CH_2HO}\end{matrix}\right.} + \underset{\text{Oxygen.}}{\mathrm{O_2}} = \underset{\text{Formic acid.}}{\left\{\begin{matrix}\mathrm{H}\\\mathrm{COOH}\end{matrix}\right.} + \underset{\text{Water.}}{\mathrm{H_2O}}$$

Formic acid can also be prepared from sugar by oxidation with sulphuric acid and black oxide of manganese; but the best method is to heat a mixture of oxalic acid and glycerin in a flask to 105°; a condenser is attached, and a liquid containing about 50 per cent. of formic acid distils over. The glycerin remains unaltered.

$$\underset{\text{Oxalic acid.}}{\left\{\begin{matrix}\mathrm{COOH}\\\mathrm{COOH}\end{matrix}\right.} = \underset{\text{Formic acid.}}{\left\{\begin{matrix}\mathrm{H}\\\mathrm{COOH}\end{matrix}\right.} + \underset{\text{Carbon dioxide.}}{\mathrm{CO_2}}$$

Properties of formic acid.—A clear, colourless liquid, with a very penetrating odour, boils at 101°; in its concentrated state it produces a blister when painted or rubbed on the skin. The wheals produced on the skin by the sting of the stinging nettle are due to the injection beneath the skin of small quantities of formic acid, from the hair of the stinging glands penetrating the skin.

Test for formic acid.—An ammoniacal solution of silver nitrate is reduced to the metallic state on warming with formic acid, the silver forming a mirror-like deposit on the sides of the test-tube.

Acetic acid ($HC_2H_3O_2$, or $\left\{\begin{matrix}\mathrm{CH_3}\\\mathrm{COOH}\end{matrix}\right.$).— There are two principal methods by which acetic acid is made: (i) The oxidation of alcohol; (ii) the dry or destructive distillation of wood. *Vinegar* is obtained by the former process; *pyroligneous acid*, or crude ~~acetic acid, by the latter.~~

Brown or *malt vinegar* is prepared by exposing beer, mixed with a little yeast, to the air; under the influence of a ferment, *mycoderma aceti*, the alcohol of the beer becomes oxidised to acetic acid.

$$\underset{\text{Alcohol.}}{\left\{\begin{matrix}CH_3\\CH_2HO\end{matrix}\right.} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Acetic acid.}}{\left\{\begin{matrix}CH_3\\COOH\end{matrix}\right.} + \underset{\text{Water.}}{H_2O}.$$

The vinegar so prepared contains about $5\frac{1}{2}$ per cent of acetic acid; a small quantity of sulphuric acid is added at the last to destroy the ferment, and so prevent any further changes from taking place in the vinegar. It is to this development of acetic acid that the souring of beer is due when exposed to the air.

White-wine vinegar is prepared by the oxidation of the alcohol contained in the light white wines; the oxidation is facilitated by allowing the wine to trickle over the surface of wood-shavings contained in towers; in this way the alcohol of the wine becomes freely exposed to the action of the oxygen of the air, and so is rapidly converted into acetic acid.

Acetic acid may be prepared from ordinary alcohol by distilling it with potassium bichromate and sulphuric acid; the two last-mentioned bodies liberate oxygen, which in the nascent state immediately oxidises the alcohol to acetic acid, which then distils over.

Dry or destructive distillation of wood.—Although wood contains no acetic acid, yet it contains the elements necessary for the formation of that body, and under the influence of dry heat, without exposure to air, a re-arrangement of the elements of the wood takes place, with the formation of several fresh bodies, amongst which is acetic acid. This process is the dry

W

or destructive distillation of wood, and if the products are collected in different portions, as they distil over, a rough separation of them is effected, since the bodies with low boiling-points will distil before those with higher boiling-points. Thus the first portion of the distillate from the destructive distillation of wood consists of impure methyl alcohol, or *wood spirit*; next comes over impure acetic acid, or *pyroligneous acid*; *creasote* and other bodies distil over afterwards; and lastly *wood tar*.

To obtain pure acetic acid from the pyroligneous acid, the latter is neutralised with sodium carbonate to form sodium acetate; the solution is then concentrated by evaporation, and, on cooling, crystals of sodium acetate separate out, leaving tarry and other impurities in the mother liquor. The crystals of sodium acetate are carefully heated, so as to expel any tar carried down with them, and the sodium acetate distilled with sulphuric acid, when pure acetic acid will be obtained as a distillate.

$$\underset{\text{Sodium acetate.}}{2NaC_2H_3O_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Acetic acid.}}{2HC_2H_3O_2} + \underset{\text{Sodium sulphate.}}{Na_2SO_4}$$

$C_2H_3O_2$

Properties of acetic acid.—Acetic acid is a clear, colourless liquid, with a penetrating, pleasant acid odour, and an acid taste. The pure acid applied to the skin produces a blister. Ordinary acetic acid (*Acidum aceticum*) is a mixture of acetic acid and 3 water, containing about 33 per cent. of real acid. Glacial acetic acid (*Acidum aceticum glaciale*) is pure acetic acid, and solidifies to a crystalline mass at temperatures below 15·5°; boils at 118°.

Three derivatives of acetic acid (chloracetic acids) are obtained by the action of chlorine on acetic acid, 1, 2, or 3 atoms of hydrogen being displaced from the acetic acid molecule, according to the amount of chlorine used. The acids are respectively called monochloracetic acid, dichloracetic acid, and trichloracetic acid.

$\left\{\begin{array}{l}CH_3\\COOH\end{array}\right.$	$\left\{\begin{array}{l}CH_2Cl\\COOH\end{array}\right.$	$\left\{\begin{array}{l}CHCl_2\\COOH\end{array}\right.$	$\left\{\begin{array}{l}CCl_3\\COOH\end{array}\right.$
Acetic acid.	Monochloracetic acid.	Dichloracetic acid	Trichloracetic acid.

Tests for acetic acid and acetates.—(i) If an acetate is boiled with sulphuric acid, the odour of acetic acid is evolved.

(ii) If an acetate is boiled with sulphuric acid and alcohol, the sweet smell of ethyl acetate (acetic ether) is obtained.

(iii) If ferric chloride is added to a solution of a neutral acetate, a blood-red colour is produced, due to the formation of ferric acetate; the colour is discharged by the addition of strong hydrochloric acid.

(iv) If a dry acetate be heated in a test-tube, the characteristic odour of acetone is evolved (*see* page 399).

Butyric acid $\left(HC_4H_7O_2, \text{ or } \left\{\begin{array}{l}C_3H_7\\COOH\end{array}\right.\right)$.—This acid is contained in human perspiration, and in rancid butter. It is prepared, as a rancid-smelling oily fluid, by the oxidation of butyl alcohol with potassium bichromate and sulphuric acid.

$$\underset{\text{Butyl alcohol.}}{C_4H_9HO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Butyric acid.}}{HC_4H_7O_2} + \underset{\text{Water.}}{H_2O}$$

Butyric acid can also be obtained from lactic acid by a fermentation process (*see* page 440).

Two varieties of butyric acid exist, normal or fermentation butyric acid $\left(\left\{\begin{array}{l}CH_3\\CH_2\\CH_2\\COOH\end{array}\right.\right)$, and isobutyric acid $\left(\begin{cases} CH(CH_3)_2 \\ COOH \end{cases}\right)$,—sometimes called **dimethylacetic** acid.

Palmitic acid $\left(\begin{cases} C_{15}H_{31} \\ COOH \end{cases}\right)$.—This acid is found in spermaceti, beeswax, palm oil, etc. It is prepared by saponifying palm oil by boiling with caustic soda, when a soap, sodium palmitate, is formed, together with glycerin; the soap is separated by throwing in salt, and finally, on decomposing the soap by boiling with dilute sulphuric acid, sodium sulphate and palmitic acid are formed.

Palmitic acid may be written $H(C_{16}H_{31}O_2)$. The equations of the above reactions are as follows:—

$$\underset{\substack{\text{Glyceryl palmitate,} \\ \text{palmitin,} \\ \text{or palm oil.}}}{C_3H_5(C_{16}H_{31}O_2)_3} + \underset{\substack{\text{Sodium} \\ \text{hydrate.}}}{3NaHO} = \underset{\substack{\text{Sodium palmitate} \\ \text{or soap.}}}{3Na(C_{16}H_{31}O_2)} + \underset{\text{Glycerin.}}{C_3H_5(HO)_3}$$

$$\underset{\text{Soap.}}{2NaC_{16}H_{31}O_2} + \underset{\substack{\text{Sulphuric} \\ \text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sodium} \\ \text{sulphate.}}}{Na_2SO_4} + \underset{\text{Palmitic acid.}}{2HC_{16}H_{31}O_2}$$

A second plan is to decompose a natural fat containing the acid with superheated steam, when the free fatty acid and glycerin are formed.

$$\underset{\text{Palm oil.}}{C_3H_5(C_{16}H_{31}O_2)_3} + \underset{\text{Steam.}}{3H_2O} = \underset{\text{Palmitic acid.}}{3HC_{16}H_{31}O_2} + \underset{\text{Glycerin.}}{C_3H_5(HO)_3}$$

Palmitic acid is a white crystalline solid, insoluble in water, soluble in boiling alcohol and in ether. Melts at 62°.

Margaric acid $\left(\left\{\begin{matrix}C_{16}H_{33}\\ COOH\end{matrix}\right.\right)$ does not seem to occur in natural fats, but can be prepared synthetically.

Stearic acid $\left(\left\{\begin{matrix}C_{17}H_{35}\\ COOH\end{matrix}\right.\right)$ occurs in beef-suet, mutton-suet, cacao butter. It is prepared from these fats by processes similar to those under palmitic acid. Stearic acid closely resembles palmitic acid, but melts at 69°. Both acids are extensively used for the manufacture of candles.

A third acid, which is a liquid, is commonly found associated with palmitic and stearic acids in the natural fats, this is oleic acid.

Oleic acid $\left(\left\{\begin{matrix}C_{17}H_{33}\\ COOH\end{matrix}\right.\right)$.—This is not, strictly speaking, a fatty acid, but belongs to a different series—the acrylic series. It occurs in olive and almond oil. When pure, it solidifies in white crystals at 14°.

FATS AND FIXED OILS.

C_3H_5 + fatty ac rad

A fat or oil is a compound of the radicle glyceryl ~~with the acid radicle of one of the higher~~ fatty acids. The large majority of fats and oils consist of the radicle glyceryl united with the oleic, stearic, and palmitic radicles. The compound of glyceryl and the oleic radicle is glyceryl oleate or *olein;* the compound of glyceryl and the stearic radicle is glyceryl stearate or *stearin;* and the compound of glyceryl and the palmitic radicle is glyceryl palmitate or *palmitin.* As the glyceryl radicle is trivalent, and the fatty acid radicles are univalent, it follows that three equivalents of the latter are required to saturate one of the former; the formulæ of these fats and oils are, therefore, as follows:—

Glyceryl oleate or olein	$C_3H_5(C_{18}H_{33}O_2)_3$.	C_3H_5(Ol
Glyceryl stearate or stearin	$C_3H_5(C_{18}H_{35}O_2)_3$.	C_3H_5(S
Glyceryl palmitate or palmitin	$C_3H_5(C_{16}H_{31}O_2)_3$.	C_3H_5(P

Olein is a liquid, stearin and palmitin are solids; therefore the larger the proportion of olein in a mixed fat the softer it will be; and the larger the proportion of stearin (which is harder than palmitin) the harder the mixed fat will be.

Olein is the chief constituent of olive oil and almond oil, and is also contained in castor oil. *Stearin* forms the bulk of beef-suet and mutton-suet. *Palmitin* is present in palm oil. Human fat is a mixture of olein, stearin, and palmitin. *Margarin*, which was formerly believed to be a simple fat, is now known to be a mixture of stearin and palmitin.

Olive oil is a type of the non-drying oils, *i.e.* oils which, when exposed to the air, become thick and acid, but do not harden. Linseed, poppy, and hemp oils, which are glycerides of linoleic acid, dry up to a hard varnish, and are termed drying oils.

SOAPS AND SAPONIFICATION.

A soap is a compound of a metal with one of the radicles of oleic, stearic, or palmitic acid, and is therefore obtained by the displacement of the glyceryl of an oil or fat by a metal. The following list shows the composition of the commonly used soaps:—

Common, yellow, or hard soap is *sodium oleate*	$NaC_{18}H_{33}O_2$
Soft soap is *potassium oleate* . . .	$KC_{18}H_{33}O_2$
Curd soap is *sodium stearate* . . .	$NaC_{18}H_{35}O_2$

Saponification is the process by which oils or fats are converted into soaps, and consists in decomposing the oil or fat with an alkali, when double decomposition takes place, resulting in the formation of a soap and glycerin.

Hard soap.—This is prepared by boiling olive oil, cocoanut oil, suet, etc., with caustic soda, when double decomposition occurs as follows :—

$$\underset{\text{Glyceryl oleate.}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\text{Sodium hydrate.}}{3NaHO} = \underset{\text{Sodium oleate.}}{3NaC_{18}H_{33}O_2} + \underset{\text{Glycerin.}}{C_3H_5(HO)_3}$$

When the process of saponification is completed, common salt is added to separate the soap from the glycerin ; the soap being insoluble in a solution of common salt, it is thrown out of solution on the addition of the salt, and rises to the surface of the liquid, when it can be removed.

Soft soap.—This is prepared by boiling olive oil and other fats with caustic potash, when double decomposition occurs as follows :—

$$\underset{\text{Glyceryl oleate.}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\text{Potassium hydrate.}}{3KHO} = \underset{\text{Potassium oleate.}}{3KC_{18}H_{33}O_2} + \underset{\text{Glycerin.}}{C_3H_5(HO)_3}$$

Common salt cannot be used to throw this soap out of solution, as it would convert it into the soda soap ; the solution is therefore evaporated to a soft consistence, the glycerin being left in the soap.

The term saponification, originally applied to the decomposition of the fats by boiling with a caustic alkali by which a soap was formed, is now extended so that it includes the decomposition of any ester by an alkali, *e.g.*,

$$\underset{\text{Ethyl chloride.}}{C_2H_5Cl} + \underset{\text{Potassium hydrate.}}{KHO} = \underset{\text{Potassium chloride.}}{KCl} + \underset{\text{Alcohol.}}{C_2H_5HO}$$

although no soap is formed.

Lactic acid $\left(HC_3H_5O_3 \text{ or } \left\{\begin{matrix}CH_2HO\\CH_2\\COOH\end{matrix}\right.\right)$.—It will be seen from the formula given below that this acid can be prepared from propionic acid by the substitution of hydroxyl (HO) for one atom of hydrogen, and is therefore hydroxypropionic acid.

H_8
H_6
$_2OH$

$\left\{\begin{matrix}C_2H_5\\COH\end{matrix}\right.$

$$\underset{\text{Propionic acid.}}{\left\{\begin{matrix}C_2H_5\\COOH\end{matrix}\right.} \qquad \underset{\text{Lactic or hydroxypropionic acid.}}{\left\{\begin{matrix}C_2H_4(HO)\\COOH\end{matrix}\right.}$$

An isomer of this acid exists known as fermentation lactic acid $\left(\left\{\begin{matrix}CH_3\\CHOH\\COOH\end{matrix}\right.\right)$.

A third isomer of lactic acid is the *sarcolactic acid* found in muscle.

Preparation of ordinary or fermentation lactic acid.—This acid is best obtained by the process known as the *lactic acid fermentation* of sugar, which is effected by the action of the ferment, *penicillium glaucum*, on either glucose or milk sugar. Under the influence of this ferment, both these sugars split up into lactic acid; the glucose molecule becoming resolved into two molecules of lactic acid, thus:

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\text{Lactic acid;}}{2C_3H_6O_3}$$

the milk-sugar molecule is resolved into four molecules of lactic acid—

$$\underset{\text{Lactose or milk sugar.}}{C_{12}H_{22}O_{11}, H_2O} = \underset{\text{Lactic acid.}}{4C_3H_6O_3}$$

The production of lactic acid by fermentation is best effected by taking a mixture of sugar, mouldy cheese (the mould of which is *penicillium glaucum*), chalk, and water, and leaving the mixture for some time in a warm place; the lactic acid as it is formed is converted by the chalk into calcium lactate, which is deposited as a crystalline mass. From the calcium lactate the lactic acid may be set free by the addition of sulphuric or oxalic acid; on filtering from the insoluble calcium sulphate or oxalate, and evaporating the filtrate, the lactic acid is obtained as a syrupy liquid.

If the fermentation is allowed to continue too long, then the lactic acid becomes decomposed by a further fermentative process into butyric acid, thus:

$$\underset{\text{Lactic acid.}}{2C_3H_6O_3} = \underset{\text{Butyric acid.}}{C_4H_8O_2} + \underset{\text{Carbon dioxide.}}{2CO_2} + \underset{\text{Hydrogen.}}{2H_2}$$

Ordinary lactic acid has no action on polarized light, and its zinc salt crystallises with three molecules of water ($Zn(C_3H_5O_3)_2 + 3H_2O$); 1 part of the salt requires 58 parts of water for its solution.

The isomer obtained from flesh (*sarcolactic acid*) is dextrorotatory. Its zinc salt has the formula $Zn(C_3H_5O_3)_2 + 2H_2O$, and 1 part of the salt dissolves in 17 of water.

The souring of milk on exposure to the air is due to the conversion of the milk sugar into lactic acid, the fermentation being induced by the spores of *penicillium glaucum*, which are always present in the air, settling on the surface of the exposed milk.

2. DIBASIC ORGANIC ACIDS.

Oxalic acid $\left(H_2C_2O_4 \text{ or } \begin{cases} COOH \\ COOH \end{cases}\right)$.—This acid is present in the form of potassium and calcium salts in a few plants, such as the wood-sorrel, rhubarb, and common dock. There is not, however, a sufficient quantity of it in these plants to render its extraction from them a commercial success, and it is therefore obtained by an artificial process. It may be prepared—

(i) In the form of its sodium salt by passing carbon dioxide over carefully heated metallic sodium.

$$\underset{\text{Sodium.}}{2Na} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{2CO_2} = \underset{\substack{\text{Sodium}\\\text{oxalate.}}}{Na_2C_2O_4}.$$

(ii) It may also be prepared by boiling cane sugar with strong nitric acid, some of the oxygen of which oxidises the sugar to oxalic acid.

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + \underset{\text{Oxygen.}}{9O_2} = \underset{\text{Oxalic acid.}}{6H_2C_2O_4} + \underset{\text{Water.}}{5H_2O}$$

(iii) On the manufacturing scale, oxalic acid is prepared from sawdust. The process is carried out on a large scale by heating sawdust to a temperature of 204° with caustic soda on iron plates, care being taken not to use sufficient heat to char the sawdust; the sodium oxalate is then extracted by means of boiling water, and decomposed by slaked lime into the insoluble calcium oxalate and caustic soda; the latter can then be used for heating with a fresh portion of sawdust.

$$\underset{\text{Sodium oxalate.}}{Na_2C_2O_4} + \underset{\text{Slaked lime.}}{Ca(HO)_2} = \underset{\text{Calcium oxalate.}}{CaC_2O_4} + \underset{\text{Caustic soda.}}{2NaHO}$$

The calcium oxalate is then decomposed with sulphuric acid and water, with formation of insoluble calcium sulphate and soluble oxalic acid; on filtering from the calcium sulphate, and concentrating the filtrate by evaporation, crystals of oxalic acid are deposited.

$$\underset{\text{Calcium oxalate.}}{CaC_2O_4} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Oxalic acid.}}{H_2C_2O_4} + \underset{\text{Calcium sulphate.}}{CaSO_4}$$

Properties of oxalic acid ($H_2C_2O_4 + 2H_2O$).—Oxalic acid is a white crystalline solid, with a very acid taste; it is an irritant poison, the antidote for it being chalk or lime-water, either of which neutralises the oxalic acid, and forms the insoluble calcium oxalate; on gently heating, water is evolved, and the anhydrous acid ($H_2C_2O_4$) sublimes.

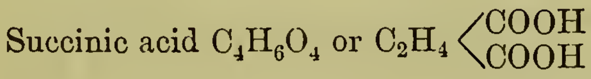
Salt of sorrel ($KHC_2O_4, H_2C_2O_4 + 2H_2O$) is an acid potassium oxalate combined with oxalic acid; it exists in the wood sorrel, and may be made by one-fourth neutralising oxalic acid with potassium carbonate; salt of sorrel and oxalic acid are both used for removing ink-stains from linen, the tannate of iron of the ink-stain being soluble in a solution of oxalic acid. Heat decomposes oxalic acid into water and the two oxides of carbon; a similar decomposition, but at a lower temperature, takes place when oxalic acid is heated with strong sulphuric acid (*see* page 157). Oxalates of the metals when heated yield carbonates, with evolution of carbon monoxide; thus:

$$\underset{\text{Calcium oxalate.}}{CaC_2O_4} = \underset{\text{Calcium carbonate.}}{CaCO_3} + \underset{\text{Carbon monoxide.}}{CO}$$

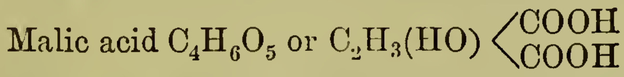
Tests for oxalic acid.—(i) If a solution of oxalic acid be neutralised with ammonia, and calcium chloride be added, a white precipitate of calcium oxalate will be thrown down; this precipitate is insoluble in acetic acid, but is soluble in hydrochloric acid.

(ii) When boiled with strong sulphuric acid, oxalic acid and the oxalates evolve CO and CO_2.

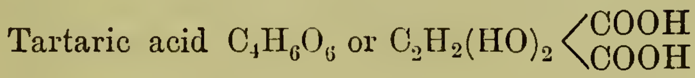
Succinic acid $\left(H_2C_4H_4O_4 \text{ or } C_2H_4\left\langle\begin{array}{l}COOH\\COOH\end{array}\right.\right)$. —This acid can be obtained from amber by heat, hence its name (from *succinum*, amber). Although not employed at all in medicine, it is of interest on account of its relationship to malic and tartaric acids, as will be seen from the following formulæ:—



Succinic acid $C_4H_6O_4$ or $C_2H_4\left\langle\begin{array}{l}COOH\\COOH\end{array}\right.$



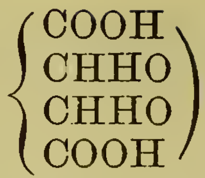
Malic acid $C_4H_6O_5$ or $C_2H_3(HO)\left\langle\begin{array}{l}COOH\\COOH\end{array}\right.$



Tartaric acid $C_4H_6O_6$ or $C_2H_2(HO)_2\left\langle\begin{array}{l}COOH\\COOH\end{array}\right.$

Malic acid is therefore hydroxysuccinic acid, and tartaric is dihydroxysuccinic or hydroxymalic acid. Succinic acid is formed in small quantities in the alcoholic fermentation. It crystallises in colourless prisms, melting at 180°; it readily sublimes.

Malic acid $\left(H_2C_4H_4O_5 \text{ or } C_2H_3(HO)\left\langle\begin{array}{l}COOH\\COOH\end{array}\right.\right)$. —This acid is present in the free state in apples, pears, cherries, berries of the mountain ash, and various other fruits; it is also present in considerable quantities in green garden rhubarb, the sourness of which is due to malic acid. It is not used in medicine, but is of interest as being intermediate in composition between succinic and tartaric acids (*see* above).



Tartaric acid $\left(H_2C_4H_4O_6 \text{ or } \left\{\begin{matrix}COOH\\ CHHO\\ CHHO\\ COOH\end{matrix}\right.\right)$.—This acid occurs as potassium acid tartrate (cream of tartar) in grapes, tamarinds, pine-apples, and several other fruits. It is deposited as *argol* during the fermentation of grape juice; for although the potassium acid tartrate is soluble in the grape juice, it is insoluble in alcohol, and is therefore precipitated as the grape sugar becomes converted into alcohol. *Argol* consists of potassium acid tartrate coloured with some of the colouring matter of the wine; it also constitutes the *crust*, formed as a sediment, in old port and other wines. *Cream of tartar*, or *bitartrate of potash*, as it is sometimes called, is argol deprived of its colouring matter by means of animal charcoal and recrystallisation.

Preparation.—Tartaric acid is prepared by dissolving cream of tartar in boiling water, and adding chalk till effervescence ceases, when one-half of the tartaric radicle is precipitated as calcium tartrate, the other half remaining in solution as potassium tartrate.

$$\underset{\substack{\text{Potassium}\\ \text{acid tartrate.}}}{2KHC_4H_4O_6} + \underset{\substack{\text{Calcium}\\ \text{carbonate.}}}{CaCO_3} = \underset{\substack{\text{Calcium}\\ \text{tartrate.}}}{CaC_4H_4O_6} + \underset{\substack{\text{Potassium}\\ \text{tartrate.}}}{K_2C_4H_4O_6} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Calcium chloride is then added to decompose the potassium tartrate, so that the whole of the cream of tartar is converted into the insoluble calcium tartrate.

$$\underset{\substack{\text{Potassium}\\ \text{tartrate}}}{K_2C_4H_4O_6} + \underset{\substack{\text{Calcium}\\ \text{chloride.}}}{CaCl_2} = \underset{\substack{\text{Calcium}\\ \text{tartrate.}}}{CaC_4H_4O_6} + \underset{\substack{\text{Potassium}\\ \text{chloride}}}{2KCl}$$

The calcium tartrate is finally decomposed with sulphuric acid and water, with the production of insoluble calcium sulphate and soluble tartaric acid; on filtering from the calcium sulphate, and concentrating the filtrate by evaporation, crystals of tartaric acid are deposited.

$$\underset{\substack{\text{Calcium}\\\text{tartrate.}}}{CaC_4H_4O_6} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Tartaric}\\\text{acid.}}}{H_2C_4H_4O_6} + \underset{\substack{\text{Calcium}\\\text{sulphate.}}}{CaSO_4}$$

Properties.—Tartaric acid is a white crystalline solid, with a very acid taste. Three isomeric varieties of tartaric acid exist, viz. dextro-tartaric acid and lævo-tartaric acid, a solution of the former twisting a ray of polarised light to the right, and of the latter to the left: ordinary tartaric acid is dextro-tartaric acid. *Racemic acid* is a mixture of the two varieties, and, in the form of the acid potassium salts, exists in some varieties of grapes: racemic acid has no action on polarised light. The third isomeric (*meso-tartaric*) acid is also without action on polarised light, but its inactivity is due to its internal structure.

Tests for tartaric acid.—(i) If to a solution of tartaric acid carefully neutralised with ammonia some silver nitrate be added, a white precipitate of silver tartrate is thrown down; on heating the mixture, a precipitate of metallic silver forms as a mirror-like deposit on the sides of the test-tube.

(ii) When stirred with a solution of potassium sulphate tartaric acid gives a white crystalline precipitate.

(iii) When heated with strong sulphuric acid, a tartrate chars and evolves the odour of burnt sugar.

3. Tribasic Organic Acids.

Citric acid $\left(H_3C_6H_5O_7 \text{ or } \left\{\begin{matrix} CH_2\ COOH \\ CHO\ COOH \\ CH_2\ COOH \end{matrix}\right.\right)$.—This acid is present in lemons, limes, currants, gooseberries, raspberries, etc. It is prepared from lemon-juice or lime-juice by first boiling the juice and filtering from any suspended matters, and then adding chalk until effervescence ceases; the precipitated calcium citrate is collected and decomposed with sulphuric acid in a manner similar to that employed in the preparation of tartaric acid.

Properties and test.—Citric acid is a white crystalline solid, with a very acid taste. The best test for the solid acid is the peculiar way in which it chars when treated with strong sulphuric acid; it first turns of a pale lemon colour, passing successively to a darker yellow colour, a sherry colour, a port colour, and finally becoming black.

It gives no mirror with silver salts, and no precipitate with potassium sulphate.

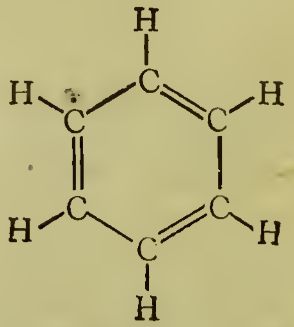
C_6H_6

CHAPTER IX.

BENZENE DERIVATIVES, OR THE AROMATIC GROUP.

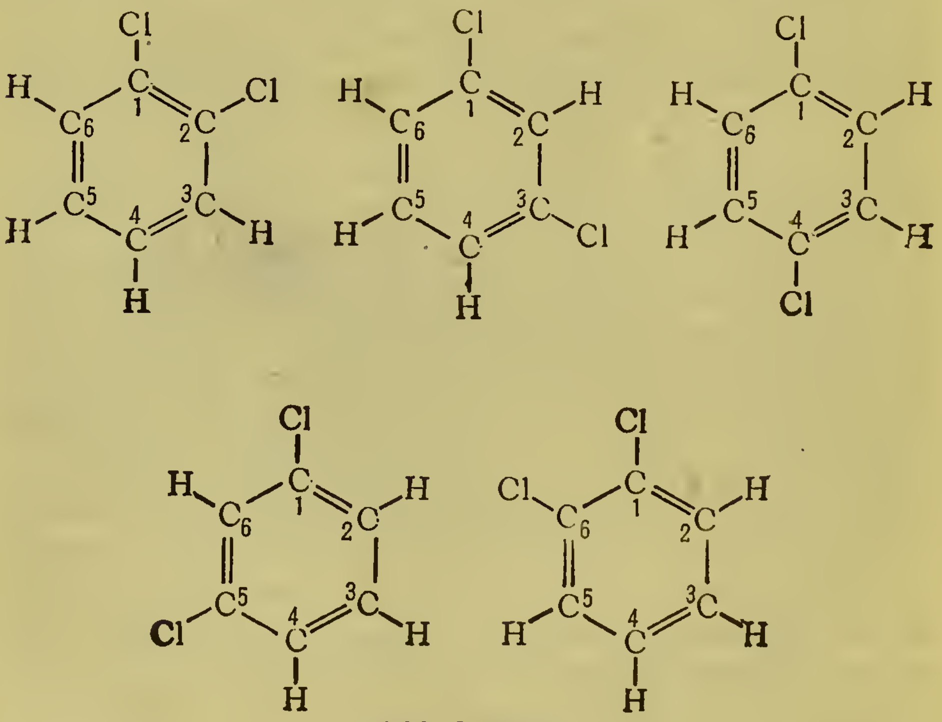
Benzene — Toluene — Nitrobenzene — Phenol or Carbolic Acid—Sulphocarbolic Acid—Picric Acid—Resorcin—Essential Oil of Bitter Almonds—Benzoic Acid—Hippuric Acid—Salicylic Acid — Gallic Acid — Pyrogallic Acid — Tannin — Terpenes—Camphor.

The *aromatic* or *closed chain* bodies present a remarkable contrast in many of their reactions and properties to the fatty or open chain bodies which we have discussed in the previous pages. As the latter may be looked upon as the derivatives, more or less direct, of marsh gas, so the aromatic bodies may be considered as derivatives of the hydrocarbon benzene. Many of them have fragrant odours, as oil of bitter almonds, nitrobenzene, benzoic acid, etc., hence the name of *aromatic* bodies. The parent substance benzene (C_6H_6) is an eminently unsaturated hydrocarbon; as carbon is a tetrad the six carbon atoms have twenty-four points to which elements can attach themselves; only six of these are occupied by atoms of hydrogen. Several formulæ have been proposed for benzene, but the one usually adopted we owe to Kekulé, who in 1865 proposed his celebrated ring formula for benzene. According to this theory the six carbon atoms are supposed to be arranged at the six angles of a hexagon, and to be alternately, doubly and singly linked. This, as will be seen in the graphic formula given, leaves six affinities free for the six hydrogen atoms—



Kekulé's ring formula for benzene.

This formula explains most of the reactions of benzene; for instance, as all the hydrogen atoms are similarly combined, as regards the carbon atoms, if we replace *one* hydrogen atom by chlorine or bromine (it matters not which hydrogen atom is replaced), the resulting monochlorbenzene will be the same in every case; accordingly we find only one monochlorbenzene known. If, however, we replace *two* atoms of hydrogen by two atoms of chlorine, three modifications, as shown below, are possible, and only three:



Dichlorbenzenes.

Thus numbering the atoms of carbon, we have the chlorine atoms attached to 1·2 consecutive, 1·3 alternate, 1·4 opposite; it is obvious that 1·5 is the same as 1·3, and 1·6 the same as 1·2. Accordingly we find three, and only three, dichlorbenzenes known. These are generally named 1·2 ortho (o), 1·3 meta (m), and 1·4 para (p) derivatives.

In the same way, 3 trichlor-, 3 tetrachlor-, 1 pentachlor-, and 1 hexchlor-benzenes are possible; in

C_6H_6

every case agreeing with the number of derivatives hitherto discovered.

Benzene (C_6H_6), often called benzol; this substance can be prepared—

(i) By heating acetylene to redness in a tube of hard glass.

$$\underset{\text{Acetylene.}}{3C_2H_2} = \underset{\text{Benzene.}}{C_6H_6}$$

(ii) By distilling benzoic acid with lime.

$$\underset{\substack{\text{Benzoic}\\\text{acid.}}}{\left\{\begin{matrix}C_6H_5\\COOH\end{matrix}\right.} + \underset{\text{Lime.}}{CaO} = \underset{\substack{\text{Calcium}\\\text{carbonate.}}}{CaCO_3} + \underset{\text{Benzene.}}{C_6H_6}$$

(iii) On the large scale it is manufactured from coal tar. When coal tar is subjected to fractional distillation, the portion which comes over below 170° is known as "light oil;" on fractionating this light oil, the portion which distils over below 140° contains the benzene. This portion is treated consecutively with dilute sulphuric acid and with caustic soda, and repeatedly washed; the neutral oil is then distilled, and the portion coming over between 80°–90° collected; it is then cooled to −12°, pressed, and finally distilled, the portion boiling 80°–81° being almost pure benzene.

Properties.—Benzene is a thin, colourless, limpid liquid, with a peculiar odour. Its sp. gr. is ·885; boils at 80·5°; solidifies at 6°. It is very inflammable, burning with a smoky flame on account of the large amount of carbon it contains. It is a powerful solvent of fats, and is on this account commonly employed for removing grease; it is almost insoluble in water, but mixes readily with alcohol and ether.

Toluene or **methylbenzene** ($C_6H_5.CH_3$).—This body is commonly known as *toluol.* It is contained in the coal-tar distillate, and passes over between 100° and 120°. It is a liquid, smelling like benzene, and may be obtained by the substitution of methyl for chlorine in chlorbenzene. This is effected by distilling together chlorbenzene, methyl iodide, and sodium.

$$\underset{\text{Chlorbenzene.}}{C_6H_5Cl} + \underset{\text{Methyl iodide.}}{CH_3I} + \underset{\text{Sodium.}}{2Na} = \underset{\text{Toluene.}}{C_6H_5.\,CH_3} + \underset{\text{Sodium chloride.}}{NaCl} + \underset{\text{Sodium iodide.}}{NaI}$$

Nitrobenzene ($C_6H_5NO_2$).—This body is also known as *nitrobenzol* and *essence of mirbane.* It is obtained by the action of strong nitric acid on benzene, the mixture being subsequently poured into water.

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Nitrobenzene.}}{C_6H_5NO_2} + \underset{\text{Water}}{H_2O}$$

$C_6H_5OH.$

Properties.—Nitrobenzene is a yellow liquid; sp. gr. 1·2; boiling at 205°; and possessing a strong odour resembling that of the *essential oil of bitter almonds*, and is on this account used for flavouring and perfuming. It is a poisonous substance, and is extensively employed in commerce in the manufacture of aniline (*see* page 460). Di-nitro ($C_6H_4(NO_2)_2$) and tri-nitro ($C_6H_3(NO_2)_3$) benzenes have also been prepared.

Phenol or **carbolic acid** (C_6H_5HO).—This body, which is the ordinary carbolic acid, is also known as *phenic acid.* It is contained in coal tar, from which it is obtained for commercial purposes from that portion of coal tar distilling between 180° and 190°. It may be obtained in a chemically pure state by the withdrawal of carbon dioxide from salicylic acid, which is effected by heating salicylic acid with quicklime.

$$\underset{\text{Salicylic acid.}}{\left\{\begin{array}{l}C_6H_4HO\\COHO\end{array}\right.} + \underset{\text{Lime.}}{CaO} = \underset{\text{Carbolic acid.}}{C_6H_5HO} + \underset{\text{Calcium carbonate.}}{CaCO_3}$$

Properties.—Carbolic acid is, in the pure state, a colourless crystalline body, but it soon assumes a pink colour. It is soluble in 15 parts of water, and readily soluble in alcohol, ether, and glycerin (*Glycerinum acidi carbolici*). If solid carbolic acid is mixed with a small quantity of water it liquefies, 100 parts of the acid and 10 parts of water forming *Acidum carbolicum liquefactum.* It possesses a characteristic odour and taste, somewhat resembling creasote. It is a powerful antiseptic on account of its germicidal properties. It is a corrosive and irritant poison. It will be noticed that phenol is the hydrate of the radicle phenyl (C_6H_5), just as ordinary alcohol is the hydrate of the radicle ethyl (C_2H_5); it differs, however, from ordinary alcohol in being much more acid in its character; thus, it dissolves readily in potassium hydrate, forming a carbolate or phenate (C_6H_5OK); moreover, it does not contain the group (CH_2HO) characteristic of a primary alcohol. On the other hand, it is not a true acid, as it does not contain the group oxatyl (COOH).

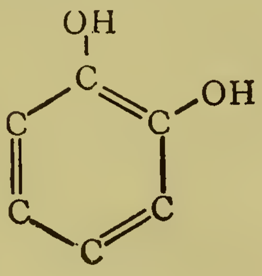
Tests.—(i) Carbolic acid gives, with bromine water, a white precipitate of tribromphenol ($C_6H_2Br_3HO$). This constitutes a very delicate test for carbolic acid, and is the best method for its detection in the urine in cases of carbolic acid poisoning, and in cases of absorption of carbolic acid from wounds washed with carbolic acid lotion. (ii) Ferric chloride gives a violet colour with a solution of carbolic acid (*see* p. 457).

Sulphocarbolic acid ($C_6H_4(HO)SO_3H$).—This is prepared by dissolving carbolic acid in strong sulphuric acid. By mixing it with metallic hydrates or carbonates, sulphocarbolates are formed. Two of these salts are used in medicine, viz. sodium sulphocarbolate ($C_6H_4(HO)SO_3Na$), and zinc sulphocarbolate.

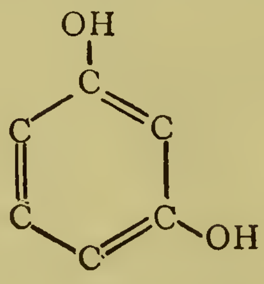
$C_6H_2(NO_2)_3OH$ = Picric Ac.

Trinitrophenol or **picric acid** ($C_6H_2(NO_2)_3HO$).—This is obtained by dropping carbolic acid into fuming nitric acid. It forms yellow crystals, known as *carbazotic acid* or *picric acid;* it is very bitter; its salts are explosive; it is used as a dye.

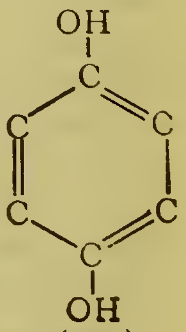
Resorcin ($C_6H_4(HO)_2$).—This body is dihydroxybenzene. Three such isomeric bodies exist, according to the relative positions of the hydroxyl groups in the benzene ring, viz. (the hydrogen atoms are omitted):



(*ortho*)
Catechol
(or pyrocatechin).



(*meta*)
Resorcinol.



(*para*)
Hydroquinone.

Of these, only the meta derivative is used in medicine.

Resorcinol or resorcin is prepared by fusing benzene-disulphonate of potassium with caustic potash.

$$C_6H_4\begin{cases}SO_3K\\SO_3K\end{cases} + 2KHO = C_6H_4(HO)_2 + 2K_2SO_3$$

Potassium benzene-disulphonate. Potassium hydrate. Resorcin. Potassium sulphite.

It is a white crystalline substance, soluble in water, alcohol, and ether. It gives a dark violet colour with ferric chloride, and a white precipitate with bromine water.

The para derivative, hydroquinone, is largely used as a developer in photography.

Pyrogallol or **pyrogallic acid** is a trihydroxybenzene (the HO groups being in the positions 1, 2, 3); it sublimes when gallic acid is heated.

$$\left\{\begin{array}{l} C_6H_2(HO)_3 \\ COOH \end{array}\right. = CO_2 + C_6H_3(HO)_3$$

It forms colourless, very light crystals, melting at 115°, and very soluble in water; when mixed with an alkaline hydrate the solution absorbs oxygen, rapidly turning almost black. 4 Pyro O N.

Benzoic aldehyde or **essential oil of bitter almonds** $\left(\begin{array}{l} C_6H_5 \\ COH \end{array}\right)$.—This is obtained from the glucoside amygdalin present in the bitter almond seeds, by digesting the bitter almonds with water and afterwards distilling. The bitter almond seeds contain a ferment *emulsin* or *synaptase*, which, in presence of water, causes the amygdalin to decompose into the essential oil of bitter almonds, hydrocyanic acid, and glucose.

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Essential oil of bitter almonds.}}{C_7H_6O} + \underset{\text{Hydrocyanic acid.}}{HCN} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

The essential oil of bitter almonds therefore contains a considerable quantity of hydrocyanic acid (4 to 8 per cent.), unless specially purified from it. It may be freed from the hydrocyanic acid by distillation with slaked lime and ferrous chloride, by which means the volatile hydrocyanic acid is converted into the non-volatile calcium ferrocyanide. If the essential oil of bitter almonds is exposed to the air it absorbs oxygen, the benzoic aldehyde becoming converted into benzoic acid, which is deposited as white crystals.

$$\underset{\text{Benzaldehyde.}}{2\left\{\begin{matrix}C_6H_5\\COH\end{matrix}\right.} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Benzoic acid.}}{2\left\{\begin{matrix}C_6H_5\\COHO\end{matrix}\right.}$$

When reduced by sodium amalgam, benzaldehyde forms benzyl alcohol.

$$\underset{\text{Benzaldehyde.}}{\left\{\begin{matrix}C_6H_5\\COH\end{matrix}\right.} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Benzyl alcohol.}}{\left\{\begin{matrix}C_6H_5\\CH_2HO\end{matrix}\right.}$$

Benzaldehyde is a thin, colourless liquid; sp. gr. 1·05; boils at 180°; it does not reduce Fehling's copper solution; it is much used for flavouring.

Benzoic acid $\left(HC_7H_5O_2 \text{ or } \left\{\begin{matrix}C_6H_5\\COOH\end{matrix}\right.\right)$.—This acid may be prepared (i) from gum benzoin, which contains from 12 to 15 per cent. of it, by heating the crushed benzoin, when the benzoic acid sublimes, or more economically by boiling the crushed benzoin with slaked lime and water, when the benzoic acid is extracted as the soluble calcium benzoate.

$$\underset{\text{Benzoic acid.}}{2HC_7H_5O_2} + \underset{\text{Slaked lime.}}{Ca(HO)_2} = \underset{\text{Calcium benzoate.}}{Ca(C_7H_5O_2)_2} + \underset{\text{Water.}}{2H_2O}$$

From the filtrate benzoic acid is precipitated by the addition of hydrochloric acid.

$$\underset{\substack{\text{Calcium}\\\text{benzoate.}}}{Ca(C_7H_5O_2)_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Benzoic}\\\text{acid.}}}{2HC_7H_5O_2} + \underset{\substack{\text{Calcium}\\\text{chloride.}}}{CaCl_2}$$

(ii) Benzoic acid may be prepared by the oxidation of oil of bitter almonds (*see* above).

(iii) Benzoic acid may also be obtained from hippuric acid, which can be extracted from the urine of cows or horses, by boiling that acid with hydrochloric acid, when it takes up a molecule of water.

$$\underset{\substack{\text{Hippuric}\\\text{acid.}}}{\left\{\begin{matrix}CH_2(NHC_7H_5O)\\COOH\end{matrix}\right.} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Amidoacetic}\\\text{acid.}}}{\left\{\begin{matrix}CH_2(NH_2)\\COOH\end{matrix}\right.} + \underset{\text{Benzoic acid.}}{HC_7H_5O_2}$$

(iv) By the action of sodium and carbon dioxide on monobrombenzene.

$$\underset{\text{Brombenzene.}}{C_6H_5Br} + \underset{\text{Sodium.}}{2Na} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} = \underset{\substack{\text{Sodium}\\\text{bromide.}}}{NaBr} + \underset{\substack{\text{Sodium}\\\text{benzoate.}}}{\left\{\begin{matrix}C_6H_5\\COONa\end{matrix}\right.}$$

Benzoic acid forms glistening crystals with a characteristic odour, slightly soluble in water, melting at 120°, subliming at 125°. The vapour produces violent coughing.

Ferric chloride gives a flesh-coloured precipitate with a benzoate.

Salicylic acid or **hydroxybenzoic acid** $\left(\left\{\begin{matrix}C_6H_4(HO)\\COOH\end{matrix}\right.\right)$.—Two kinds of salicylic acid occur in commerce, namely, the *natural* and *artificial* salicylic acids. The natural salicylic acid is obtained from oil of winter green or methyl salicylate, by distilling it with caustic soda, when methyl alcohol distils over and sodium salicylate is left behind. If the sodium salicylate is dissolved in water, salicylic acid can be precipitated by the addition of hydrochloric acid to the solution. Artificial salicylic acid is prepared from carbolic acid. It will be seen that if carbon dioxide is added to the molecule of carbolic acid salicylic acid is produced; thus:

$$\underset{\substack{\text{Carbolic}\\\text{acid.}}}{C_6H_6O} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} = \underset{\substack{\text{Salicylic}\\\text{acid.}}}{C_7H_6O_3}$$

This is effected by converting the carbolic acid into sodium carbolate by the addition of caustic soda, and then heating the sodium carbolate in a stream of carbon dioxide at 200°, when it becomes converted into sodium salicylate.

$$\underset{\substack{\text{Sodium}\\\text{carbolate.}}}{C_6H_5NaO} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} = \underset{\substack{\text{Sodium}\\\text{salicylate.}}}{NaC_7H_5O_3}$$

Salicylic acid is precipitated from an aqueous solution of the sodium salicylate by the addition of hydrochloric acid.

Properties.—Salicylic acid is a white solid, free from smell, slightly soluble in cold water and readily soluble in hot water, alcohol, and ether. It is an antiseptic. It is largely used in medicine in the form of its sodium salt, the preparation of which has been described in the two processes given above.

Tests.—(i) A solution of salicylic acid gives, with ferric chloride, a violet colour. (ii) Salicylic acid, heated with quicklime, evolves the odour of carbolic acid, the quicklime extracting the carbon dioxide from the salicylic acid, and so reducing it to carbolic acid. (iii) With strong sulphuric acid and a little potassium nitrite solution, a permanent red colour is produced (phenol gives a red colour, which turns through green to blue).

Gallic acid or **tri-hydroxybenzoic acid,** or **di-hydroxysalicylic acid** $\left(\left\{\begin{matrix} C_6H_2(HO)_3 \\ COHO \end{matrix}\right.\right)$.—Gallic acid occurs in small quantity in oak galls, but is generally prepared from tannic acid by the union of that body with the elements of water. As tannic acid is contained to a considerable extent in oak galls, gallic acid is prepared by boiling the crushed galls with dilute sulphuric acid for about half an hour, when the tannin unites with the elements of water and forms gallic acid. If the liquid is filtered while hot, it deposits crystals of gallic acid on cooling.

Test.—A solution of gallic acid gives, with ferric chloride, a bluish-black precipitate of ferric gallate.

Tannin or **tannic acid** ($C_{14}H_{10}O_9$).—This substance is a constituent of oak galls, from which it is obtained by macerating the galls in a mixture of ether, alcohol and water. The strained aqueous liquor, if evaporated, deposits tannin. The relationship of tannin to gallic acid is represented in the following equation, which shows that two molecules of gallic acid, deprived of one molecule of water, yield tannin.

$$\underset{\text{Gallic acid.}}{2C_7H_6O_5} \quad - \quad \underset{\text{Water.}}{H_2O} \quad = \quad \underset{\text{Tannin.}}{C_{14}H_{10}O_9}$$

Tests.—(i) A solution of tannic acid gives, with ferric chloride, a dark bluish-black precipitate of ferric tannate resembling in appearance the precipitate of ferric gallate. (ii) An aqueous solution of tannin precipitates an aqueous solution of gelatine. This test serves to distinguish tannic acid from gallic acid, as the latter does not precipitate gelatine.

TERPENES.

Terpenes of the formula $C_{10}H_{16}$ are isomeric hydrocarbons occurring as volatile oils in plants, from which they may be obtained by a process of distillation. The commonest terpene is oil of turpentine; other terpenes isomeric with this are the volatile or essential oils of lemon, orange, citron and bergamot.

Essential oil of turpentine ($C_{10}H_{16}$) is also known as oil of turpentine, spirits of turpentine, turpentine, and "turps." It is prepared by distillation from the crude turpentine or oleo-resin, obtained from various species of pine trees; the volatile oil of turpentine distilling over, common resin is left in the retort.

Camphor ($C_{10}H_{16}O$).—This substance is a partially-oxidised terpene; it is a solid volatile substance obtained from the camphor plant.

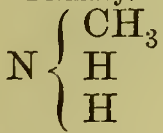
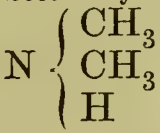
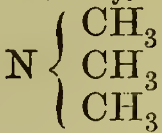
CHAPTER X.

AMINES, AMIDES, AMIDO ACIDS, ALKALOIDS.

Amines—Trimethylamine—Anilin—Amides—Urea—Uric Acid—Amido Acids—Glycocine—Hippuric Acid—Glycocholic Acid—Sarcosine—Tyrosine—Leucine—Alkaloids.

An amine may be regarded as ammonia, in which one, two, or three atoms of hydrogen have been replaced by unoxidised radicles, such as methyl, ethyl, phenyl, etc.; or it may be looked upon as derived from a hydrocarbon by replacing an atom of hydrogen by the amido group (NH_2); thus, from benzene (C_6H_6) we obtain anilin ($C_6H_5NH_2$).

A *primary amine* is one produced by the displacement of one atom of hydrogen of the ammonia by an alcohol radicle; a *secondary amine* by the displacement of two atoms of hydrogen; a *tertiary amine* by the displacement of all the hydrogen. Thus:—

Primary.	Secondary.	Tertiary.
 $N\begin{cases}CH_3\\H\\H\end{cases}$	 $N\begin{cases}CH_3\\CH_3\\H\end{cases}$	 $N\begin{cases}CH_3\\CH_3\\CH_3\end{cases}$
Methylamine.	Dimethylamine.	Trimethylamine.

Very few of the amines have, at present, any medical interest. They closely resemble in their general properties ammonia. Thus, they have a strong odour and alkaline action; they combine with acids to form salts and give precipitates with platinum chloride. Their vapours burn in the air.

Trimethylamine $\left(N\begin{cases}CH_3\\CH_3\\CH_3\end{cases}\right)$ is a body with a strong fishy odour, and is contained in herring-brine.

The amines are prepared by digesting the iodides of the radicles, in sealed tubes, with alcoholic ammonia, at 100°.

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\substack{\text{Ethylamine}\\\text{hydriodide.}}}{NH_2C_2H_5HI}$$

On boiling the hydriodide with caustic potash the amine is set free.

Anilin, or phenylamine $\left(N\left\{\begin{array}{l}C_6H_5\\H\\H\end{array}\right.\right)$.—This important amine is prepared by the action of reducing agents on nitrobenzene ($C_6H_5NO_2$); this is generally carried out by exposing nitrobenzene to the action of iron filings and acetic acid.

$$\underset{\text{Nitrobenzene.}}{C_6H_5NO_2} + \underset{\text{Hydrogen.}}{3H_2} = \underset{\text{Anilin.}}{N\left\{\begin{array}{l}C_6H_5\\H\\H\end{array}\right.} + \underset{\text{Water.}}{2H_2O}$$

Anilin, when first prepared, is a colourless liquid, boils at 184·5°, specific gravity 1·036; it gradually assumes a brownish colour on exposure to air. Anilin is a powerful base. When acted upon by oxidising substances it furnishes a number of coloured bodies, well known as anilin dyes.

Heated with solid mercuric chloride, anilin forms a dark red mass, soluble in alcohol to a magenta-coloured solution.

Heated with chloroform, alcohol, and caustic potash, a body of extremely disagreeable odour is produced—phenyl isocyanide (C_6H_5NC); this can be used as a test for chloroform or anilin.

An amide may be regarded as ammonia in which one or more atoms of hydrogen have been replaced by the acid or oxidised radicles, as acetyl (C_2H_3O), or

N_2H_2 N_2H_2 = $Co(NH_2)_2$
H_2 H_2

they may be considered as acids in which one or more hydroxyl groups (HO) have been replaced by amido groups (NH_2); thus, from acetic acid $\left(\left\{\begin{matrix}CH_3\\COOH\end{matrix}\right.\right)$ we have acetamide $\left(\left\{\begin{matrix}CH_3\\CONH_2\end{matrix}\right.\right)$, and from carbonic acid $\left(CO\left\{\begin{matrix}HO\\HO\end{matrix}\right.\right)$, urea or carbamide $\left(CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.\right)$. They can be prepared from the ammonium salts of organic acids by the abstraction of water; thus:

$$\underset{\text{Ammonium acetate.}}{NH_4C_2H_3O_2} \quad - \quad \underset{\text{Water.}}{H_2O} \quad = \quad \underset{\text{Acetamide.}}{N\left\{\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right.}$$

They are also obtained by the action of ammonia on acid chlorides; thus:

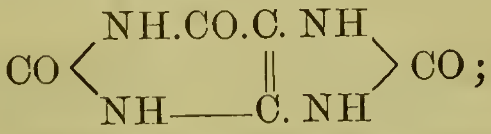
$$\underset{\text{Ammonia.}}{NH_3} \quad + \quad \underset{\substack{\text{Acetyl}\\\text{chloride.}}}{C_2H_3OCl} \quad = \quad \underset{\text{Acetamide.}}{C_2H_3ONH_2} \quad + \quad \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl}$$

They are usually neutral bodies combining with both bases and acids.

Acetamide is a colourless, crystalline solid, melting at 81°, boils at 222°. As usually obtained, it has an intolerable odour of mice; it is soluble in water and alcohol.

Carbamide or **urea.**—This important substance has already been described in Chapter III. in connection with the cyanates (*see* p. 374).

Uric acid ($C_5H_4N_4O_3$), or



$$CO\left\langle\begin{matrix}NH.CO.C.NH\\ \| \\ NH——C.NH\end{matrix}\right\rangle CO;$$

formerly also called lithic acid, is a normal constituent of the urine. *Sodium biurate* constitutes the gouty concretions in joints known as chalk stones. Ammonium urate is the chief constituent of the solid excrement of snakes.

Uric acid can be prepared from urine by acidifying with hydrochloric acid, when the uric acid separates out in crystals. It can be obtained in a purer state by boiling boa's excrement with potash, filtering and pouring the filtrate into dilute hydrochloric acid, when the uric acid is precipitated as a white powder. It has also been prepared artificially by heating glycol with urea. It is not a true acid, as it does not contain the oxatyl group, but it acts like a weak dibasic acid. It is almost insoluble in water. The acid is soluble in caustic potash and caustic soda. It is closely related to the alkaloids, theobromine and theine.

Test.—If a few drops of strong nitric acid be added to some solid uric acid in a dish, and heat gently applied until all the nitric acid be driven off, a reddish coloured residue (alloxan) will be left. If, when the dish is cold, a few drops of solution of ammonia are added to this, a beautiful crimson purple colour is developed, due to the production of murexid by the action of the ammonia on alloxan. This test for uric acid is, on this account, known as the *murexid* test.

AMIDO ACIDS.

The amido acids are acids in which the hydrogen or hydroxyl of the acid has been replaced by the amido group (NH_2); thus, from acetic acid $\left(\left\{\begin{matrix}CH_3\\COOH\end{matrix}\right.\right)$ we have glycocoll $\left(\left\{\begin{matrix}CH_2NH_2\\COOH\end{matrix}\right.\right)$, from oxalic acid $\left(\left\{\begin{matrix}COOH\\COOH\end{matrix}\right.\right)$ we have oxamic acid $\left(\left\{\begin{matrix}CONH_2\\COOH\end{matrix}\right.\right)$.

Glycocine, glycine, glycocoll, or **amido-acetic acid** $\left(\left\{\begin{matrix}CH_2(NH_2)\\COOH\end{matrix}\right.\right)$. — This body may be obtained by the action of ammonia on chloracetic acid.

$$\underset{\text{Chloracetic acid.}}{\left\{\begin{matrix}CH_2.Cl\\COOH\end{matrix}\right.} + \underset{\text{Ammonia.}}{NH_3} = \underset{\text{Amidoacetic acid.}}{\left\{\begin{matrix}CH_2(NH_2)\\COOH\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl}$$

Glycocine enters into the composition of hippuric acid and of glycocholic acid, one of the bile acids. It is a solid crystalline substance with a sweetish taste, soluble in water.

Hippuric acid $\left(\left\{\begin{matrix}CH_2(NH.C_7H_5O\\COHO\end{matrix}\right.\right)$ is benzamidoacetic acid, and is resolved by boiling with strong hydrochloric acid into benzoic acid and glycocine (*see* benzoic acid, page 455). It can be prepared from cows' and horses' urine by boiling with lime, filtering and pouring the filtrate into hydrochloric acid.

Glycocholic acid, present as sodium glycocholate in bile, is a compound of glycocine and cholic acid; by boiling glycocholic acid with hydrochloric acid it splits up into glycocine and cholic acid.

Sarcosine or **methyl-glycocine** $\left(\left\{\begin{matrix}CH_2(NH.CH_3)\\COOH\end{matrix}\right.\right)$.—This body is glycocine, from which one atom of hydrogen of the amidogen has been displaced by methyl. Since glycocine is prepared by acting on chloracetic acid with ammonia, so sarcosine may be made by acting on chloracetic acid with methylamine, that is, with ammonia from which one atom of hydrogen has been displaced by methyl.

$$\underset{\text{Chloracetic acid.}}{\left\{\begin{matrix}CH_2Cl\\COOH\end{matrix}\right.} + \underset{\text{Methylamine.}}{NH_2.CH_3} = \underset{\text{Sarcosine.}}{\left\{\begin{matrix}CH_2(NH.CH_3)\\COOH\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl}$$

Sarcosine is not met with in the animal body, but is a product of the decomposition of creatine.

Tyrosine ($C_9H_{11}NO_3$).—This body consists of amido-propionic acid from which one atom of hydrogen of the amidogen has been displaced by the radicle hydroxyphenyl (C_6H_4HO).

$$\underset{\text{Amido-propionic acid.}}{\left\{\begin{array}{l}C_2H_4(NH_2.)\\COOH\end{array}\right.} \qquad \underset{\text{Tyrosine.}}{\left\{\begin{array}{l}C_2H_4(NH.C_6H_4HO)\\COOH\end{array}\right.}$$

Tyrosine is occasionally found in the urine together with leucine in connection with certain diseases of the liver; they are also both found among the products of pancreatic digestion.

Leucine or **amido caproic acid** $\left(\left\{\begin{array}{l}C_5H_{10}(NH_2)\\COOH\end{array}\right.\right)$. — This body consists of caproic acid $\left(\left\{\begin{array}{l}C_5H_{11}\\COOH\end{array}\right.\right)$, from the molecule of which one atom of hydrogen has been displaced by amidogen. It is obtained by the action of ammonia on bromo-caproic acid.

$$\underset{\text{Bromo-caproic acid.}}{\left\{\begin{array}{l}C_5H_{10}.Br\\COOH\end{array}\right.} + \underset{\text{Ammonia.}}{NH_3} = \underset{\text{Leucine.}}{\left\{\begin{array}{l}C_5H_{10}(NH_2)\\COOH\end{array}\right.} + \underset{\text{Hydrobromic acid}}{HBr}$$

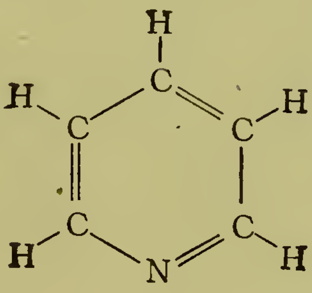
Leucine is occasionally found in the urine in connection with certain diseases of the liver; it is one of the antecedents of urea.

VEGETABLE ALKALOIDS.

These bodies are organic bases, resembling the alkalies in their properties of turning red litmus paper blue, and of uniting with acids to form salts; hence the derivation of the name "alkaloid," from *alkali*, and εἶδος, likeness. All alkaloids contain nitrogen, and are, in fact, derivatives of ammonia, the hydrogen of which has been partially or entirely displaced by various radicles. Alkaloids unite with acids to form crystalline salts.

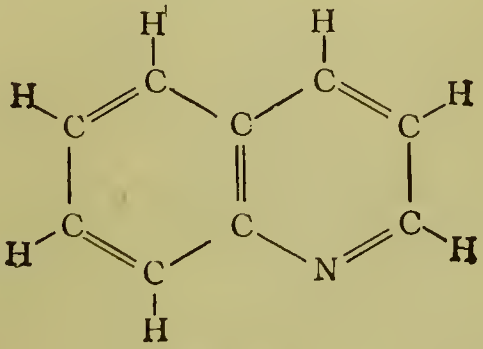
Most of the alkaloids are solid, crystalline, and non-volatile. Two, conine and nicotine, which contain no oxygen, are volatile liquids. A few have been prepared synthetically, as muscarin, conine, theobromine, and thein, but the constitution of the majority of the alkaloids is unknown.

Some are believed to be derivatives of pyridine, a liquid found in coal tar and in bone oil. Its constitution may be considered as benzene, in which one of the CH groups is replaced by nitrogen.



Pyridine.

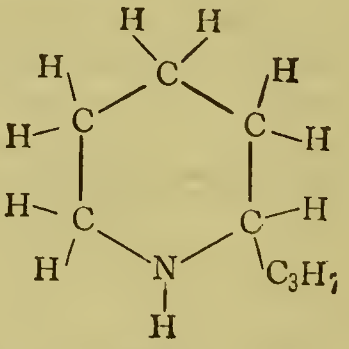
Some, as the quinine alkaloids, are closely connected with quinolin, an oil also found in coal tar and bone oil, which may be looked upon as two benzene rings, having two carbon atoms in common, in which one CH group has been replaced by one atom of nitrogen.



Quinolin.

Muscarin ($C_5H_{15}NO_3$) is the alkaloid contained in the poisonous mushroom, the *fly agaric*. It is also formed under certain conditions in putrefying *animal* tissues, so that it may be classed as an animal alkaloid, or *ptomaine*. It has been prepared artificially from cholin by the action of nitric acid. Cholin may be considered as ammonium hydrate (NH_4HO), in which three atoms of hydrogen are replaced by three methyl (CH_3) groups, and the fourth by hydroxyethyl (C_2H_4HO). Thus, the constitutional formula of cholin is $N(CH_3)_3(C_2H_4HO)HO$. By the action of nitric acid the hydroxyethyl is converted into dihydroxyethyl ($C_2H_3(HO)_2$), so that the formula of muscarin is $N(CH_3)_3(C_2H_3(HO)_2)HO$.

Conine ($C_8H_{17}N$) is contained in the seeds of the hemlock, from which it can be obtained by distillation with caustic soda; it is a colourless oil, boiling at 167° and readily soluble in water. It has been prepared artificially and shown to be a propyl (C_3H_7) derivative of piperidine (a substance occurring in pepper), and to have the constitution—



Conine.

Theobromine ($C_7H_8N_4O_2$), **thein,** or **caffein** ($C_8H_{10}N_4O_2$).—These alkaloids can be prepared from uric acid, the constitution of which was given in the previous chapter (page 461). Theobromine is the essential alkaloid in cocoa. Thein and caffein (which seem to be identical) are found in tea and coffee. If uric acid be treated with sodium amalgam, one atom of oxygen is replaced by an atom of hydrogen and an atom of hydrogen is removed, a new substance, xanthin, being formed.

$$\underset{\text{Uric acid.}}{C_5H_4N_4O_3} + H_2 = \underset{\text{Water.}}{H_2O} + \underset{\text{Xanthin.}}{C_5H_4N_4O_2}$$

By subjecting xanthin to a well-known process, two atoms of hydrogen are replaced by two methyl (CH_3) groups, and we have dimethylxanthin or theobromine ($C_5H_2(CH_3)_2N_4O_2$) ; by repeating the process another hydrogen is similarly replaced and trimethylxanthin or thein ($C_5H(CH_3)_3N_4O_2$) is formed.

Alkaloids whose constitution is, at present, unknown.

Morphine or **morphia** ($C_{17}H_{19}NO_3$, H_2O).—This alkaloid exists in opium in combination with meconic acid as *meconate of morphine*; a fair sample of opium contains from 8 to 12 per cent. of morphine. It is extracted by the following process :

(i) The opium is macerated in water and exhausted by percolation, by which means an aqueous extract of the meconate of morphine is obtained.

(ii) To this aqueous extract calcium chloride is added, when the meconic acid is precipitated as calcium meconate, the soluble hydrochlorate of morphine remaining in solution.

(iii) The liquid is filtered, and the filtrate, containing the hydrochlorate of morphine, is decolorised by boiling with animal charcoal.

(iv) The liquid is filtered from the animal charcoal, and evaporated to a low bulk; it is then set aside to cool, when it deposits crystals of the hydrochlorate of morphine.

(v) To obtain the free alkaloid, solution of ammonia is added to a strong aqueous solution of the hydrochlorate, when the morphine is thrown down as a white precipitate, the ammonia uniting with the hydrochloric acid.

Morphine hydrochlorate or **hydrochlorate of morphia** ($C_{17}H_{19}NO_3$, HCl).—This compound is prepared in the process just described.

Morphine acetate or **acetate of morphia** ($C_{17}H_{19}NO_3$, $C_2H_4O_2$).—This compound is prepared by dissolving the free alkaloid (precipitated by ammonia from the hydrochlorate) in acetic acid. Morphine acetate is the salt generally employed for hypodermic injection.

Tests for morphine.—(i) Ferric chloride gives, with a neutral solution of a morphine salt, a dingy blue colour. In the cases of the acetate and meconate of morphine, this blue colour is more or less neutralised by the production of the red colour that ferric chloride gives with an acetate and meconate.

(ii) Strong nitric acid gives an orange-red colour with morphine and its salts; this colour can also be obtained by the addition of sufficient nitric acid to a strong solution of a morphine salt.

(iii) Sulphomolybdic acid (made by warming strong H_2SO_4 with a little solid Am_2MoO_4), rubbed with morphine or any of its salts in the solid state, gives a dark crimson colour, changing after a short time to a sapphire blue; this constitutes a very delicate test for morphine.

Detection of opium.—Apart from its characteristic smell, analytical evidence of the presence of opium is gained by obtaining the reactions for morphine (as detailed above) and for meconic acid. The reaction for meconic acid is that it gives a blood-red colour with ferric chloride, which colour is not discharged either by the addition of hydrochloric acid or of solution of mercuric chloride; hence distinguishing it from similar red colours given by ferric chloride with acetates and sulphocyanides (*see* pages 372, 434).

Apomorphine ($C_{17}H_{17}NO_2$).—The molecule of this body differs from that of morphine by containing one molecule of water less. It is prepared by heating morphine with strong hydrochloric acid, when the elements of water are withdrawn from the morphine, and the hydrochlorate of apomorphine remains. This alkaloid possesses entirely different physiological properties to those of morphine; it is a very powerful and rapid emetic, and has none of the narcotic properties of morphine and its salts.

Codeine ($C_{18}H_{21}NO_3$, H_2O).—This is one of the alkaloids of opium; it is closely related to morphine, being *methyl-morphine*; that is, it consists of morphine, from the molecule of which one atom of hydrogen has been displaced by the radicle methyl, as shown in the following formulæ:

Morphine—$C_{17}H_{19}NO_3$, H_2O
Codeine or methyl-morphine—$C_{17}H_{18}(CH_3)NO_3$, H_2O.

Quinine or **quinia** ($C_{20}H_{24}N_2O_2$, $3H_2O$).—This, together with other alkaloids, exists in the different cinchona barks in combination with kinic acid. It is extracted by the following process:

(i) The powdered cinchona bark is exhausted by percolation with water acidulated with hydrochloric acid, by which means the quinine is removed in solution as hydrochlorate of quinine.

(ii) The solution is decolorised by means of animal charcoal.

(iii) The quinine is precipitated from the solution of the hydrochlorate by the addition of caustic soda, which sets free the quinine as a white precipitate, by uniting with the hydrochloric acid to form sodium chloride.

Sulphate of quinine.—This is the form in which quinine is generally employed in medicine; it is made by dissolving the precipitated quinine in dilute sulphuric acid. The commercial sulphate of quinine, or *disulphate of quinine*, as it is sometimes called, has the composition $(C_{20}H_{24}N_2O_2)_2$, H_2SO_4; it is only slightly soluble in water, but may be readily dissolved by the addition of a little dilute sulphuric acid, which forms the so-called neutral or soluble sulphate $(C_{20}H_{24}N_2O_2$, $H_2SO_4)$.

Tests for quinine.—(i) If to a solution of a quinine salt some chlorine water and then solution of ammonia be added, a green colour will be produced.

(ii) If the above-mentioned test be repeated, adding some potassium ferrocyanide solution before the addition of the ammonia, a red colour will be produced.

Cinchonine, *cinchonidine*, and *quinidine* are alkaloids also present in cinchona barks.

Strychnine or **strychnia** $(C_{21}H_{22}N_2O_2)$.—This alkaloid exists in nux vomica seeds in combination with igasuric acid as strychnine igasurate; another alkaloid, *brucine* or *brucia*, is also present in the seeds as brucine igasurate.

Strychnine is extracted by the following process:

(i) The crushed seeds are exhausted by maceration and percolation with rectified spirit, and from the tincture so obtained the spirit is recovered by distillation.

(ii) The soft extract left after the recovery of the spirit is mixed with water, to precipitate resinous matters, and acetate of lead added to throw down colouring matter and igasurate of lead, acetate of strychnine being left in solution.

(iii) The liquid is filtered from precipitated matters, and the filtrate is concentrated by evaporation; on the addition of ammonia, strychnine is precipitated, together with brucine.

(iv) To separate the brucine from the strychnine the precipitate is dissolved in alcohol, and the solution is evaporated to a low bulk; on setting it aside to cool the strychnine crystallises out, leaving the more soluble brucine in solution in the mother liquid.

Test for strychnine.—If a little strong sulphuric acid be added to a fragment of strychnine placed on a white porcelain dish or plate, and the mixture be touched with a glass rod dipped in a solution of potassium bichromate in strong sulphuric acid (made by adding a crystal or two of the bichromate to a few drops of sulphuric acid), a beautiful dark purple or violet colour will be developed, fading after a short time to a pale red colour.

Brucine or **brucia** ($C_{23}H_{26}N_2O_4$).—The separation of this alkaloid from strychnine has been described in the process just given.

Test for brucine.—Strong nitric acid gives a bright blood-red colour with brucine and its salts.

Rarer alkaloids.—Aconitine, atropine, cocaine, hyoscyamine, veratrine, etc., are prepared by separate processes, for a description of which the student is referred to the British Pharmacopœia (1885). These rarer alkaloids are not, however, always prepared by the lengthy official processes of the B. P.; they may be obtained by the following general method:

General process for the extraction of alkaloids.—(i) The crushed roots, bark, leaves, fruits, or seeds are exhausted by maceration and percolation with alcohol containing tartaric acid; tartrates of the alkaloids being soluble in alcohol.

(ii) The alcohol is recovered by distillation, and the soft extract left is mixed with water to precipitate resinous matters.

(iii) The liquid is filtered from precipitated resinous matters, and the alkaloid precipitated by the addition of sodium carbonate.

(iv) The precipitated alkaloid is purified by solution in, and crystallisation from, a suitable solvent, such as ether, chloroform, or alcohol. If necessary, colouring matter is removed from the alkaloid by means of animal charcoal.

Liquid volatile alkaloids.—Conine (contained in the conium or hemlock plant), nicotine (contained in tobacco), and pilocarpine (contained in jaborandi leaves) are liquid volatile alkaloids; they may all be prepared by distilling the part of the plant containing the alkaloid with a dilute solution of caustic potash, when the alkaloid is set free, and being volatile distils over.

PTOMAINES OR ANIMAL ALKALOIDS.

Ptomaines are alkaloids produced by the decomposition of animal substances. The word *ptomaine*, which is derived from *πτῶμα*, a corpse, and *inus*, belonging to, was at first restricted to alkaloids produced by cadaveric decomposition; it is now also employed to designate alkaloids of animal origin formed during life as the result of chemical changes induced by some agency or other acting within the organism.

At the beginning of this century the formation of alkaloids by plants was clearly established; but until 1872 the power of producing alkaloids was believed to be restricted to plants, and not to be shared by animal organisms. Gautier, as the result of his researches on putrefying albuminous substances, was the first to clearly establish the fact that plants possess no monopoly of producing alkaloids, but that this productive power is equally shared by animal substances. The various forms of albumen are the common ancestors of alkaloids, whether animal or vegetable; and it is by various changes in the albumen molecule that animal alkaloids are produced.

CHAPTER XI.

GLUCOSIDES—RARER ORGANIC COMPOUNDS USED IN MEDICINE.

Amygdalin—Cathartic Acid—Colocynthin—Digitalin—Indican—Jalapin—Myronic Acid—Salicin—Santonin—Antifebrine—Antipyrine—Benzosol—Guaiacol—Hypnone—Ichthyol—Iodol—Naphthalene—Naphthol—Phenacetin—Saccharine—Salol—Sulphonal—Urethane.

GLUCOSIDES.

THESE are certain organic substances (nitrogenous or non-nitrogenous) derived from plants, and splitting up, when boiled with dilute sulphuric acid, or under the influence of a ferment, into *glucose* and some other substance or substances.

Amygdalin ($C_{20}H_{27}NO_{11}$).—This is a white crystalline substance present in bitter almond seeds, cherry laurel leaves, and the kernels of peaches, cherries, etc. Amygdalin is resolved, by boiling with dilute sulphuric acid, into essential oil of bitter almonds (benzoic aldehyde), hydrocyanic acid, and glucose. The same change is also produced by the action of a ferment named *emulsin* or *synaptase*, which is present, together with amygdalin, in bitter almond seeds, cherry laurel leaves, and the kernels of peaches, cherries, etc. This ferment is unable to act upon the amygdalin unless dissolved in water.

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Essential}\\ \text{oil of}\\ \text{bitter almonds.}}}{C_7H_6O} + \underset{\substack{\text{Hydrocyanic}\\ \text{acid.}}}{HCN} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

Cathartic acid.—This very complex glucoside exists in senna leaves, of which it is the active purgative principle; it is decomposed by boiling with dilute sulphuric acid into glucose and a substance named cathartogenic acid.

Colocynthin ($C_{56}H_{84}O_{23}$).—This substance is the active purgative principle of colocynth pulp; it is decomposed by boiling with dilute sulphuric acid into glucose and a resinous substance.

Digitalin ($C_{27}H_{45}O_{15}$).—This glucoside is the active principle of digitalis leaves; by boiling with dilute sulphuric acid, it is decomposed into glucose, and a substance named digitaliretin.

Indican ($C_{26}H_{31}NO_{17}$)?) occurs in the *Indigofera*, in woad and other plants; it is obtained as a yellowish bitter syrup. By boiling with dilute acids it is decomposed into indigo and a sugar (indiglucin). The name has also been erroneously applied to the substance, present in the urine, which produces indigo blue on standing; the substance in the urine is not a glucoside, but is potassium indoxyl sulphate ($K(C_8H_6N)SO_4$).

Jalapin ($C_{34}H_{56}O_{16}$).—This substance is the active purgative principle of jalap root; it is decomposed by boiling with dilute sulphuric acid, into glucose and a substance named jalapinol.

Myronic acid ($C_{10}H_{19}NS_2O_{10}$).—This acid exists as a potassium salt in black mustard seeds; the salt is decomposed by boiling with dilute sulphuric acid, and also by the action of a ferment *myrosin*, likewise contained in black mustard seeds, into volatile oil of mustard (allyl sulphocyanate), glucose, and potassium acid sulphate.

$$\underset{\substack{\text{Potassium}\\\text{myronate.}}}{KC_{10}H_{18}NS_2O_{10}} = \underset{\substack{\text{Allyl}\\\text{sulphocyanate.}}}{C_3H_5.CNS} + \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\substack{\text{Potassium}\\\text{acid sulphate.}}}{KHSO_4}$$

Salicin ($C_{13}H_{18}O_7$).—This is a crystalline bitter principle contained in the leaves and bark of the willow; it is resolved by boiling with dilute sulphuric acid into glucose and a substance named saligenin.

$$\underset{\text{Salicin.}}{C_{13}H_{18}O_7} + \underset{\text{Water.}}{H_2O} = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Saligenin.}}{C_7H_8O_2}$$

Santonin ($C_{15}H_{18}O_3$).—This glucoside is the active principle of santonica.

Rarer Organic Substances used in Medicine.

Acetanilide ($NH.C_6H_5,C_2H_3O$), also known as *antifebrin* and *phenylacetamide*, may be regarded as acetamide ($NH_2C_2H_3O$), in which one atom of hydrogen has been replaced by the radicle phenyl (C_6H_5); it is obtained by the prolonged action of glacial acetic acid on pure anilin.

$$\underset{\text{Anilin.}}{NH_2\,C_6H_5} + \underset{\text{Acetic acid.}}{HC_2H_3O_2} = \underset{\text{Acetanilide.}}{NHC_6H_5C_2H_3O} + \underset{\text{Water.}}{H_2O}$$

It forms colourless, odourless crystals, with a greasy feel and faint burning taste, not very soluble in cold water, but soluble in alcohol, ether, and chloroform. Used as an antipyretic.

Antipyrin $\left(C_6H_5N\left\{\begin{matrix}CO.CH\\NCH_3.CCH_3\end{matrix}\right.\right)$, known in the B. P. as *phenazone*, a somewhat complex benzene derivative prepared by the interaction of phenylhydrazine $\left(\begin{matrix}NH_2\\NHC_6H_5\end{matrix}\right)$ and acetoacetic ether $\left(\begin{matrix}COC_2H_5\\COOC_2H_5\end{matrix}\right)$, and subsequent methylation of the product. It is a colourless, odourless, crystalline substance, melting at 110°, readily soluble in water, alcohol, and chloroform. Used as an antipyretic.

Benzosol ($C_6H_4.O(CH_3).O(C_7H_5O)$ is *benzoylguaiacol* (*see* below), that is, one of the H atoms in guaiacol ($C_6H_4.OCH_3.OH$) has been replaced by the acid radicle benzoyl (C_7H_5O). It is a colourless, crystalline powder, melts at 59°, insoluble in water, soluble in ether and in chloroform. Used in cases of phthisis.

Guaiacol ($C_6H_4.OH.O(CH_3)$), *methyl catechol* (~~*see* page 452~~), prepared from beechwood tar creosote, is a coloured liquid of an agreeable odour; sp. gr. 1·133; readily soluble in alcohol and ether. Used in phthisis.

Hypnone.—This body is phenyl-methyl-ketone; that is, it consists of CO in union with the phenyl and methyl radicles; thus :—

$$C_6H_5—CO—CH_3$$

Hypnone.

It is obtained, by distillation, from a mixture of benzoate of calcium and acetate of calcium. At ordinary temperatures it is a colourless oily liquid, but below 14° it crystallises in white needles. It is insoluble in water, but soluble in alcohol.

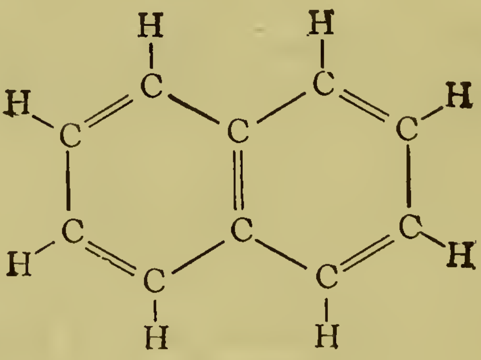
Ichthyol ($(NH_4)_2C_{28}H_{36}S_3O_6$).—This substance is an ammonium salt of sulpho-ichthyolic acid. It is obtained by treating the products of distillation of a bituminous quartz with sulphuric acid, and neutralising the sulpho-ichthyolic acid so produced with ammonia. The strata from which the bituminous quartz is obtained contain the remains of fishes and other animals, and the deposit probably consists of their decomposed and altered remains.

Iodol.—This substance is tetra-iodo-pyrrol (C_4HI_4N); that is, it is pyrrol (C_4H_5N) from the molecule of which four atoms of hydrogen have been displaced by four atoms of iodine.

It is obtained by the action of iodine on pyrrol, which is an oily liquid contained in bone-oil, produced by the dry or destructive distillation of bones.

Iodol is a brownish-white powder, insoluble in water, but soluble in glycerin, alcohol, ether, and chloroform. It is used as an antiseptic.

Naphthalene ($C_{10}H_8$).—This is a hydrocarbon, obtained as a bye-product in the preparation of coal gas; it may be regarded as two benzene rings having two carbon atoms in common.

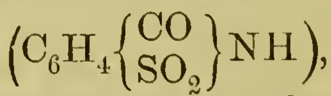


Naphthalene.

It occurs in white, shining, crystalline plates, insoluble in water, but soluble in alcohol and ether. It is an antiseptic.

β-Naphthol ($C_{10}H_7.HO$).—Two isomeric modifications, α-naphthol and β-naphthol, exist; they are derivatives of naphthalene, from the molecule of which one atom of hydrogen is displaced by hydroxyl. Naphthol occurs in white shining crystals, sparingly soluble in water, but soluble in alcohol and ether; it is a powerful antiseptic.

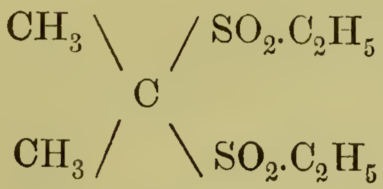
Phenacetine ($C_6H_4.OC_2H_5.NH.CH_3CO$). — A derivative of nitrophenol ($C_6H_4.NO_2.OH$), crystallises in colourless, tasteless, glistening scales, melting at 135°, not very soluble in water. An antipyretic.



Saccharin $\left(C_6H_4\left\{\begin{matrix}CO\\SO_2\end{matrix}\right\}NH\right)$, *benzoyl sulphonic imide.*—An imide may be regarded as NH_3, in which two atoms of hydrogen have been replaced by a divalent acid radicle. Sulphobenzoic acid is benzoic acid $\left(\begin{matrix}C_6H_5\\COOH\end{matrix}\right)$ in which one of the hydrogen atoms in the phenyl group is replaced by the radicle (SO_2OH). $C_6H_4\left\{\begin{matrix}SO_2OH\\COOH\end{matrix}\right.$; the imide is formed by replacing two atoms of hydrogen in ammonia by the divalent group $\left(C_6H_4\left\{\begin{matrix}SO_2\\CO\end{matrix}\right.\right)$. It is obtained by a complicated series of processes from toluene and methylbenzene ($C_6H_5.CH_3$). It is a white, intensely sweet powder, slightly soluble in water, more soluble in alcohol.

Salol $\left(\begin{matrix}C_6H_4HO\\COO(C_6H_5)\end{matrix}\right)$, *phenyl salicylate.*—It is a white crystalline substance, insoluble in water, but soluble in alcohol; it possesses antiseptic and antipyretic properties.

Sulphonal.—This body is a derivative of methane (CH_4), from the molecule of which two atoms of hydrogen are displaced by two equivalents of methyl (CH_3), and the other two atoms by two equivalents of the ethyl sulphonic group ($C_2H_5.SO_2$); the constitution of sulphonal is therefore diethylsulphondimethyl methane; thus:



Sulphonal.

It is produced by the oxidation of a mixture of ethyl-mercaptan and acetone. It occurs in white tabular crystals, tasteless and odourless, slightly soluble in water, and freely soluble in alcohol and ether. It is a hypnotic.

Urethane $\left(CO\left\{\begin{matrix}NH_2\\OC_2H_5\end{matrix}\right.\right)$.—This substance is ethyl carbamate, carbamic acid being the substance intermediate between carbonic acid $\left(CO\left\{\begin{matrix}OH\\OH\end{matrix}\right.\right)$ and urea $\left(CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.\right)$; it occurs in colourless crystals, readily soluble in water. It is a hypnotic.

Part V.

CHEMICAL PROBLEMS—WEIGHTS AND MEASURES—ANALYSIS OF A SIMPLE SALT — PREPARATION OF TYPICAL SALTS, ETC.

CHEMICAL PROBLEMS.

In this section of the book, illustrations will be given of the modes of working out the various chemical problems, which for the sake of convenience will be arranged in three groups, viz. :—*Group I.* Chemical problems involving weight calculations only. *Group II.* Chemical problems involving both weight and volume calculations. *Group III.* Chemical problems involving volume calculations only.

GROUP I.—CHEMICAL PROBLEMS INVOLVING WEIGHT CALCULATIONS ONLY.

1. How many pounds of oxygen can be obtained from 100 lbs. of potassium chlorate?

The equation representing the effect of heat upon potassium chlorate shows that all the oxygen is evolved.

$$KClO_3 = KCl + 3O$$

The molecular weight of potassium chlorate is next calculated.

$$\begin{array}{lr} K & = 39 \\ Cl & = 35{\cdot}5 \\ O_3 = 16 \times 3 & = 48 \\ \hline & 122{\cdot}5 \end{array}$$

From this it is evident that 122·5 parts by weight of potassium chlorate contain 48 parts by weight of oxygen, and since all the oxygen is evolved by heat, therefore 122·5 parts by weight of potassium chlorate will evolve 48 parts by weight of oxygen, and therefore 122·5 lbs. of potassium chlorate will evolve 48 lbs. of oxygen. If 48 lbs. of oxygen can be obtained from 122·5 lbs. of potassium chlorate, how many lbs. of oxygen can be obtained from 100 lbs. of potassium chlorate?

$$122{\cdot}5 : 100 :: 48 : x$$

$x = 39{\cdot}18$, the number of lbs. of oxygen that can be obtained from 100 lbs. of potassium chlorate.

2. How many grammes of carbon dioxide are evolved by heating 120 grammes of calcium carbonate?

The equation representing the effect of heat upon calcium carbonate shows that one molecule of calcium carbonate evolves one molecule of carbon dioxide.

$$CaCO_3 = CaO + CO_2$$

The molecular weights of these two bodies are next calculated.

$$\begin{array}{lr} Ca & = 40 \\ C & = 12 \\ O_3 = 16 \times 3 & = 48 \\ \hline & 100 \end{array} \qquad \begin{array}{lr} C & = 12 \\ O_2 = 16 \times 2 & = 32 \\ \hline & 44 \end{array}$$

From these weights it is evident that 100 parts by weight of calcium carbonate evolve 44 parts by weight of carbon dioxide, and therefore 44 grammes of carbon dioxide are obtainable from 100 grammes of calcium carbonate. Therefore, how many grammes of carbon dioxide will be evolved from 120 grammes of calcium carbonate?

$$100 : 120 :: 44 : x$$

$x = 52{\cdot}80$, the number of grammes of carbon dioxide evolved by heating 120 grammes of calcium carbonate.

3. How many grains of sulphur dioxide are evolved by the action of 150 grains of sulphuric acid on copper?

The equation representing the action of sulphuric acid on copper shows that one molecule of sulphur dioxide is evolved from two molecules of the acid.

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

Twice the molecular weight of sulphuric acid and the molecular weight of sulphur dioxide are next calculated.

$$\begin{array}{lcr} H_2 = 1 \times 2 & = & 2 \\ S & = & 32 \\ O_4 = 16 \times 4 & = & 64 \\ \hline & & 98 \end{array} \qquad \begin{array}{lcr} S & = & 32 \\ O_2 = 16 \times 2 & = & 32 \\ \hline & & 64 \end{array}$$

$$\therefore\ 2H_2SO_4 = 98 \times 2 = 196$$

From these weights it is evident that 64 parts by weight of sulphur dioxide are evolved from 196 parts by weight of sulphuric acid, by the action of that acid on copper, and therefore 64 grains of sulphur dioxide are evolved from 196 grains of sulphuric acid. Therefore, how many grains of sulphur dioxide will be evolved from 150 grains of sulphuric acid, under similar conditions ?.

$$196 : 150 :: 64 : x$$

$x = 48{\cdot}97$, the number of grains of sulphur dioxide evolved by the action of 150 grains of sulphuric acid on copper.

4. How many pounds of sodium carbonate are required to precipitate 100 lbs. of calcium chloride ?

The equation representing the action of sodium carbonate on calcium chloride shows that one molecule of sodium carbonate is required to precipitate one molecule of calcium chloride.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

The molecular weights of calcium chloride and sodium carbonate are next calculated.

$$\begin{array}{lr} Ca & = 40 \\ Cl_2 = 35{\cdot}5 \times 2 & = 71 \\ \hline & 111 \end{array} \qquad \begin{array}{lr} Na_2 = 23 \times 2 & = 46 \\ C & = 12 \\ O_3 = 16 \times 3 & = 48 \\ \hline & 106 \end{array}$$

From these weights it is evident that 106 parts by weight of sodium carbonate are required to precipitate 111 parts by weight of calcium chloride, and therefore 106 lbs. of sodium carbonate are required to precipitate 111 lbs. of calcium chloride. Therefore, how many pounds of sodium carbonate will be required to precipitate 100 lbs. of calcium chloride ?

$$111 : 100 :: 106 : x$$

$x = 95{\cdot}49$, the number of lbs. of sodium carbonate required to precipitate 100 lbs. of calcium chloride.

5. How many grammes of nitric acid are required to convert 150 grammes of copper into copper nitrate?

The equation representing the action of nitric acid on copper shows that eight molecules of nitric acid are required to convert 3 atoms of copper into copper nitrate.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Eight times the molecular weight of nitric acid, and three times the atomic weight of copper are next calculated.

$$\begin{array}{lrl} H & = & 1 \\ N & = & 14 \\ O_3 = 16 \times 3 & = & 48 \\ \hline & & 63 \end{array} \qquad 3Cu = 63{\cdot}5 \times 3 = 190{\cdot}5$$

$$\therefore\ 8HNO_3 = 63 \times 8 = 504$$

From these weights it is evident that 504 parts by weight of nitric acid are required to convert 190·5 parts by weight of copper into copper nitrate, and therefore that 504 grammes of nitric acid are required to act upon 190·5 grammes of copper. Therefore, how many grammes of nitric acid will be required to act upon 150 grammes of copper?

$$190{\cdot}5 : 150 :: 504 : x$$

$x = 396{\cdot}85$, the number of grammes of nitric acid required to convert 150 grammes of copper into copper nitrate.

6. How many kilogrammes of mercuric iodide can be prepared from 10 kilogrammes of mercuric chloride?

The equation representing the preparation of mercuric iodide from mercuric chloride shows that one molecule of mercuric iodide is prepared from one molecule of mercuric chloride.

$$HgCl_2 + 2KI = HgI_2 + 2KCl$$

The molecular weights of mercuric chloride and mercuric iodide are next calculated.

$$\begin{array}{lr} Hg & = 200 \\ Cl_2 = 35{\cdot}5 \times 2 = & 71 \\ \hline & 271 \end{array} \qquad \begin{array}{lr} Hg & = 200 \\ I_2 = 127 \times 2 = & 254 \\ \hline & 454 \end{array}$$

From these weights it is evident that 454 parts by weight of mercuric iodide are prepared from 271 parts by weight of mercuric chloride, and therefore that 454 kilogrammes of mercuric iodide would be prepared from 271 kilogrammes of mercuric chloride. Therefore, how many kilogrammes of mercuric iodide can be prepared from 10 kilogrammes of mercuric chloride?

$$271 : 10 :: 454 : x$$

$x = 16{\cdot}75$, the number of kilogrammes of mercuric iodide that can be prepared from 10 kilogrammes of mercuric chloride.

7. Calculate the percentage of sulphur in sulphuric acid.

The molecular weight of sulphuric acid is first calculated.

$$\begin{array}{llr} H_2 = 1 \times 2 & = & 2 \\ S & = & 32 \\ O_4 = 16 \times 4 & = & 64 \\ \hline & & 98 \end{array}$$

From this molecular weight it is evident that 98 parts by weight of sulphuric acid contain 32 parts by weight of sulphur. Therefore, what amount of sulphur will 100 parts of sulphuric acid contain?

$$98 : 100 :: 32 : x$$

$x = 32{\cdot}65$, the percentage of sulphur in sulphuric acid.

8. Calculate the percentage of iron in ferric oxide.

The molecular weight of ferric oxide is first calculated.

$$\begin{array}{llr} Fe_2 = 56 \times 2 & = & 112 \\ O_3 = 16 \times 3 & = & 48 \\ \hline & & 160 \end{array}$$

From this molecular weight it is evident that 160 parts by weight of ferric oxide contain 112 parts by weight of iron. Therefore, what amount of iron will 100 parts of ferric oxide contain?

$$160 : 100 :: 112 : x$$

$x = 70{\cdot}00$, the percentage of iron in ferric oxide.

9. Calculate the percentage of carbon in starch.

The molecular weight of starch is first calculated.

$$\begin{array}{lcrcrcr} C_6 & = & 12 & \times & 6 & = & 72 \\ H_{10} & = & 1 & \times & 10 & = & 10 \\ O_5 & = & 16 & \times & 5 & = & 80 \\ \hline & & & & & & 162 \end{array}$$

From this molecular weight it is evident that 162 parts by weight of starch contain 72 parts by weight of carbon. Therefore, what amount of carbon will 100 parts of starch contain?

$$162 : 100 :: 72 : x$$

$x = 44{\cdot}44$, the percentage of carbon in starch.

10. Calculate the percentage of nitrogen in urea.

The molecular weight of urea is first calculated.

$$\begin{array}{lcrcrcr} C & & & & & = & 12 \\ H_4 & = & 1 & \times & 4 & = & 4 \\ N_2 & = & 14 & \times & 2 & = & 28 \\ O & & & & & = & 16 \\ \hline & & & & & & 60 \end{array}$$

From this molecular weight it is evident that 60 parts by weight of urea contain 28 parts by weight of nitrogen. Therefore, what amount of nitrogen will be contained in 100 parts of urea?

$$60 : 100 :: 28 : x$$

$x = 46{\cdot}66$, the percentage of nitrogen in urea.

11. Calculate the percentage of chlorine in chloroform.

The molecular weight of chloroform is first calculated.

$$\begin{array}{llr} C & = & 12 \\ H & = & 1 \\ Cl_3 = 35{\cdot}5 \times 3 & = & 106{\cdot}5 \\ \hline & & 119{\cdot}5 \end{array}$$

From this molecular weight it is evident that 119·5 parts by weight of chloroform contain 106·5 parts by weight of chlorine. Therefore, what amount of chlorine will be contained in 100 parts of chloroform?

$$119{\cdot}5 : 100 :: 106{\cdot}5 : x$$

$x = 89{\cdot}12$, the percentage of chlorine in chloroform.

Group II.—Chemical Problems involving both Weight and Volume Calculations.

For the conversion of the weights of gases into volumes, it is necessary to know either the weight of a litre of hydrogen, or the volume occupied by a gramme of hydrogen; the specific gravity of any given gas being known, it then becomes an easy matter to calculate the volume occupied by any given weight of it.

The *crith* is the weight of a litre of hydrogen at 0° C. and 760 mm. barometric pressure, and is 0·0896 of a gramme. The weight of a litre of oxygen, the specific gravity of which is 16, would be 0·0896 gramme × 16; the weight of a litre of carbon dioxide, the specific gravity of which is 22, would be 0·0896 gramme × 22; in fact, the weight of a litre of any

1 gram H @ 0 C + 760 mm – 11.2

gas is obtained by multiplying the crith by the specific gravity of the gas. The conversion of the weights of gases into volumes is, however, facilitated by bearing in mind that 1 gramme of hydrogen occupies 11·2 litres (at 0° C. and 760 mm. barometric pressure). Now, since oxygen is 16 times heavier than hydrogen, 11·2 litres of oxygen must weigh 16 times as much as the same volume of hydrogen, that is, 16 grammes; again, since carbon dioxide is 22 times heavier than hydrogen, 11·2 litres of carbon dioxide must weigh 22 times as much as the same volume of hydrogen, that is, 22 grammes. In fact, the weight of 11·2 litres of any gas at 0° C. and 760 mm. barometric pressure is obtained by expressing its specific gravity as grammes. This fact may also be stated thus: 1 *molecular weight of any gas or vapour in grammes measures* 22·4 *litres.*

1. How many litres of hydrogen will be evolved by the action of sulphuric acid on 10 grammes of zinc?

The equation representing the action of sulphuric acid on zinc shows that 2 atoms of hydrogen are liberated by the action of 1 atom of zinc on sulphuric acid.

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

The respective weights of zinc and hydrogen are—

$$Zn = 65 \qquad H_2 = 1 \times 2 = 2$$

Therefore, 2 parts by weight of hydrogen are evolved by 65 parts by weight of zinc from the sulphuric acid, and therefore 2 grammes of hydrogen are evolved by 65 grammes of zinc. Now, as the *molecular* weight of hydrogen is 2, 2 grammes of hydrogen will measure 22·4 litres, and our statement reads 65 grammes of zinc evolve 22·4 litres of hydrogen. How many litres will 10 grammes of zinc evolve?

$$65 : 10 :: 22{\cdot}4 : x$$

$x = 3{\cdot}44$ litres, the number of litres of hydrogen evolved by the action of sulphuric acid on 10 grammes of zinc.

2. How many litres of oxygen are evolved by heating 50 grammes of potassium chlorate?

The equation representing the decomposition of potassium chlorate by heat shows that 1 molecule of potassium chlorate yields 3 atoms of oxygen.

$$KClO_3 = KCl + 3O$$

The molecular weight of potassium chlorate and three times the atomic weight of oxygen are next calculated.

$$\begin{array}{lr} K & = 39 \\ Cl & = 35{\cdot}5 \\ O_3 = 16 \times 3 & = 48 \\ \hline & 122{\cdot}5 \end{array} \qquad O_3 = 16 \times 3 = 48$$

Therefore 48 parts by weight of oxygen are evolved from 122·5 parts by weight of potassium chlorate, and therefore 48 grammes of oxygen are evolved from 122·5 grammes of potassium chlorate. Now, as 1 molecular weight of oxygen (32) in grammes measures 22·4 litres; 48 grammes will measure 33·6 litres. Our statement now becomes 122·5 grammes of potassium chlorate evolve 33·6 litres of oxygen. How much will be evolved by 50 grammes?

$$122{\cdot}5 : 50 :: 33{\cdot}6 : x$$

$x = 13{\cdot}75$ litres, the number of litres of oxygen evolved by heating 50 grammes of potassium chlorate.

3. How many litres of sulphur dioxide are produced by burning 5 grammes of sulphur?

The molecular weight of sulphur dioxide

$$\begin{array}{lr} S & = 32 \\ O_2 = 16 \times 2 & = 32 \\ \hline & 64 \end{array}$$

shows that sulphur produces twice its weight of sulphur dioxide, and, therefore, 5 grammes of sulphur, when burnt, would produce 10 grammes of sulphur dioxide.

This weight of sulphur dioxide must next be converted into litres. 1 gramme of hydrogen occupies 11·2 litres, and as the specific gravity of sulphur dioxide is 32 (half its molecular weight), therefore 32 grammes of sulphur dioxide occupy 11·2 litres. Therefore, how many litres will 10 grammes of sulphur dioxide occupy?

$$32 : 10 :: 11{\cdot}2 : x$$

$x = 3{\cdot}50$ litres, the number of litres of sulphur dioxide produced by burning 5 grammes of sulphur.

4. What volume of nitrogen dioxide will be produced by the action of nitric acid on 20 grammes of copper?

The equation representing the production of nitrogen dioxide by the action of nitric acid on copper shows that 2 molecules of nitrogen dioxide are set free by 3 atoms of copper.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Three times the atomic weight of copper and twice the molecular weight of nitrogen dioxide are next calculated.

$$3Cu = 63{\cdot}5 \times 3 = 190{\cdot}5 \qquad \begin{array}{r} 2N = 14 \times 2 = 28 \\ 2O = 16 \times 2 = 32 \\ \hline 60 \end{array}$$

From these weights it is evident that 60 parts by weight of nitrogen dioxide are produced by the action of nitric acid on 190·5 parts by weight of copper; and, therefore, 60 grammes of nitrogen dioxide are evolved by means of 190·5 grammes of copper.

Now the molecular weight of nitric oxide (NO) is 30, so that 30 grammes measure 22·4 litres and 60 grammes will measure 44·8 litres. Our statement now reads 190·5 grammes of copper evolve 44·8 litres of gas; what volume will be produced by 20 grammes?

$$190{\cdot}5 : 20 :: 44{\cdot}8 : x$$

$x = 4{\cdot}7$ litres, the volume of nitrogen dioxide produced by the action of nitric acid on 20 grammes of copper.

5. What volume of methane (marsh gas will be produced by heating 30 grammes of sodium acetate with caustic soda?

The equation representing the production of methane from sodium acetate and caustic soda shows that 1 molecule of sodium acetate takes part in the production of 1 molecule of methane.

$$NaC_2H_3O_2 + NaHO = Na_2CO_3 + CH_4$$

The molecular weights of sodium acetate and methane are next calculated.

$$\begin{array}{lrl} Na & & = 23 \\ C_2 & = 12 \times 2 & = 24 \\ H_3 & = 1 \times 3 & = 3 \\ O_2 & = 16 \times 2 & = 32 \\ & & \overline{82} \end{array} \qquad \begin{array}{lrl} C & & = 12 \\ H_4 & = 1 \times 4 & = 4 \\ & & \overline{16} \end{array}$$

From these weights it is evident that 16 parts by weight of methane are obtained from 82 parts by weight of sodium acetate, and, therefore, 16 grammes of methane are obtainable from 82 grammes of sodium acetate. The molecular weight of marsh gas is 16 ∴ 16 grammes of marsh gas measure 22·4 litres, and our statement reads 82 grammes of sodium acetate yield 22·4 litres of marsh gas; how many litres will 30 grammes yield?

$$82 : 30 :: 22{\cdot}4 : x$$

$x = 8{\cdot}19$ litres, the volume of methane produced by heating 30 grammes of sodium acetate with caustic soda.

6. What volume of oxygen is required to burn 10 grammes of carbon to carbon dioxide, and what volume of carbon dioxide will be formed?

The formula of carbon dioxide (CO_2) shows that 1 atom of carbon requires 2 atoms of oxygen to form carbon dioxide. The atomic weight of carbon and twice the atomic weight of oxygen are next taken.

$$C = 12 \qquad O_2 = 16 \times 2 = 32$$

From these weights it is evident that 32 parts by weight of oxygen are required for the combustion of 12 parts by weight of carbon, and, therefore, 32 grammes of oxygen are required by 12 grammes of carbon, and 44 grammes of carbon dioxide will be formed.

Now the molecular weight of oxygen is 32, therefore, 32 grammes of oxygen measure 22·4 litres; similarly, 44 grammes of carbon dioxide measure 22·4 litres, and our statement reads 12 grammes of carbon require 22·4 litres of oxygen and furnish 22·4 litres of carbon dioxide. How many litres will be required by 10 grammes of carbon?

$$12 : 10 :: 22{\cdot}4 : x$$

$x = 18{\cdot}66$ litres, the volume of oxygen required to burn 10 grammes of carbon to carbon dioxide, and 18·66 litres of carbon dioxide will be formed.

This answer may also be obtained by using the crith (*see* p. 489).

Thus, a litre of hydrogen weighs ·0896 gramme, and a litre of oxygen $\therefore$ weighs $\cdot0896 \times 16 = 1{\cdot}434$ gramme.

Now, as above, 12 grammes of carbon required 32 grammes of oxygen $\therefore$ 10 will require $\frac{32 \times 10}{12}$ $= 26{\cdot}66$ grammes, and this occupies $\frac{1 \times 26{\cdot}66}{1{\cdot}43}$ $= 18{\cdot}6$ litres. It is obvious that the first method is simpler and shorter.

7. How many grammes of calcium carbonate will be precipitated by passing 20 litres of carbon dioxide through lime-water?

The equation representing the action of carbon dioxide on lime-water shows that 1 molecule of carbon dioxide is employed in the preparation of 1 molecule of calcium carbonate.

$$Ca(HO)_2 + CO_2 = CaCO_3 + H_2O$$

The molecular weights of carbon dioxide and calcium carbonate are next calculated.

$$\begin{array}{lr} C & = 12 \\ O_2 = 16 \times 2 & = 32 \\ & \overline{\quad 44} \end{array} \qquad \begin{array}{lr} Ca & = 40 \\ C & = 12 \\ O_3 = 16 \times 3 & = 48 \\ & \overline{\quad 100} \end{array}$$

From these weights it is evident that 44 parts by weight of carbon dioxide precipitate 100 parts by weight of calcium carbonate, and therefore 44 grammes of carbon dioxide precipitate 100 grammes of calcium carbonate.

As 44 is the molecular weight of carbon dioxide, 44 grammes of this gas measure 22·4 litres, therefore 22·4 litres of carbon dioxide precipitate 100 grammes of calcium carbonate. What weight will be precipitated by 20 litres?

$$22{\cdot}4 : 20 :: 100 : x$$

$x = 89{\cdot}28$ grammes, the weight of calcium carbonate precipitated by passing 20 litres of carbon dioxide through lime-water.

8. How many grammes of sodium chloride can be prepared from 50 litres of hydrochloric acid gas?

The formulæ of sodium chloride ($NaCl$) and hydrochloric acid gas (HCl) show that 1 molecule of the former can be prepared from 1 molecule of the latter Their molecular weights are next calculated.

$$\begin{array}{lcr} Na & = & 23 \\ Cl & = & 35{\cdot}5 \\ \hline & & 58{\cdot}5 \end{array} \qquad \begin{array}{lcr} H & = & 1 \\ Cl & = & 35{\cdot}5 \\ \hline & & 36{\cdot}5 \end{array}$$

From these weights it is noticed that 58·5 parts by weight of sodium chloride can be prepared from 36·5 parts by weight of hydrochloric acid gas, and therefore 58·5 grammes of sodium chloride can be prepared from 36·5 grammes of hydrochloric acid gas. The molecular weight of hydrogen chloride is 36·5, so 36·5 grammes measure 22·4 litres, and 22·4 litres of hydrogen chloride will form 58·5 grammes of sodium chloride. How many grammes can be prepared from 50 litres?

$$22{\cdot}4 : 50 :: 58{\cdot}5 : x$$

$x = 130{\cdot}58$ grammes, the weight of sodium chloride that can be prepared from 50 litres of hydrochloric acid gas.

9. How many grammes of ammonium chloride are required to produce 30 litres of ammonia gas?

The formulæ of ammonium chloride (NH_4Cl) and ammonia gas (NH_3) show that 1 molecule of the former yields 1 molecule of the latter. Their molecular weights are next calculated.

$$\begin{array}{llr}
N & & = 14 \\
H_4 & = 1 \times 4 & = 4 \\
Cl & & = 35{\cdot}5 \\
\hline
 & & 53{\cdot}5
\end{array}
\qquad\qquad
\begin{array}{llr}
N & & = 14 \\
H_3 & = 1 \times 3 & = 3 \\
\hline
 & & 17
\end{array}$$

We learn from these weights that 53·5 parts by weight of ammonium chloride are required to produce 17 parts by weight of ammonia gas, and therefore 53·5 grammes of ammonium chloride are required to produce 17 grammes of ammonia gas.

The molecular weight of ammonia is 17, so 17 grammes measure 22·4 litres, and 53·5 grammes of ammonium chloride yield 22·4 litres of ammonia. How many grammes will be required to produce 30 litres?

$$22{\cdot}4 : 30 :: 53{\cdot}5 : x$$

$x = 71{\cdot}65$ grammes, the weight of ammonium chloride required to produce 30 litres of ammonia gas.

Group III.—Chemical Problems involving Volume Calculations only.

The solution of problems of this class is a very simple matter. It is only necessary to write out a complete equation of the reaction involved in the problem, and to observe the relative numbers of the molecules of the gases taking part in the reaction; since the molecules of all gases occupy the same space, the relative numbers of molecules expressed in the equation represent the relative volumes of gases taking part in the reaction. It is quite immaterial whether the volumes of the gases are expressed in pints, litres, gallons, etc. (as will be seen from the following examples):

1. How many pints of oxygen are required for the combustion of 10 pints of hydrogen?

The equation representing the combustion of hydrogen is first written out.

$$\underset{\text{2 molecules.}}{2H_2} + \underset{\text{1 molecule.}}{O_2} = 2H_2O$$

From this equation it is obvious that 1 molecule of oxygen is required for the combustion of 2 molecules of hydrogen, and since the molecules of all gases occupy the same space, therefore 1 pint of oxygen will be required for the combustion of 2 pints of hydrogen, and, therefore, for the combustion of 10 pints of hydrogen, 5 pints of oxygen will be required.

2. How many litres of oxygen are required for the combustion of 5 litres of sulphuretted hydrogen?

The equation representing the combustion of sulphuretted hydrogen is first written out.

$$\underset{\text{2 molecules}}{2H_2S} + \underset{\text{3 molecules.}}{3O_2} = 2H_2O + 2SO_2$$

From this equation it is evident that 3 molecules of oxygen are required for the combustion of 2 molecules of sulphuretted hydrogen, and therefore 3 litres of oxygen are required for the combustion of 2 litres of sulphuretted hydrogen. Therefore, how many litres of oxygen will be required for the combustion of 5 litres of sulphuretted hydrogen?

3 litres of O required for combustion of 2 litres of H_2S
∴ 1½ ,, ,, ,, ,, 1 ,, ,,
∴ 7½ ,, ,, ,, ,, 5 ,, ,,

3. How many gallons of carbon dioxide are produced by burning 10 gallons of olefiant gas (ethylene)?

The equation representing the combustion of olefiant gas is first written out.

$$\underset{\text{1 molecule}}{C_2H_4} + 3O_2 = \underset{\text{2 molecules.}}{2CO_2} + 2H_2O$$

From this equation we can see that 2 molecules of carbon dioxide are produced by burning 1 molecule of olefiant gas, and therefore 2 gallons of carbon dioxide are produced by burning 1 gallon of olefiant gas.

1 gallon of C_2H_4 produces 2 gallons of CO_2
∴ 10 gallons ,, produce 20 ,, ,,

4. How many cubic feet of oxygen are required for the combustion of 2 cubic feet of marsh gas (methane)?

The equation representing the combustion of marsh gas is first written out.

$$\underset{\text{1 molecule.}}{CH_4} + \underset{\text{2 molecules.}}{2O_2} = CO_2 + 2H_2O$$

This equation clearly indicates that 2 molecules of oxygen are required for the combustion of 1 molecule of marsh gas, and therefore 2 cubic feet of oxygen are required for the combustion of 1 cubic foot of marsh gas, and therefore 4 cubic feet of oxygen will be required for the combustion of 2 cubic feet of marsh gas.

5. How many pints of air are required for the combustion of 2 pints of marsh gas?

The problem is first worked out, as in the preceding case, to ascertain the number of pints of oxygen required for the combustion of 2 pints of marsh gas; it was found that 4 pints of oxygen were required. It now remains to ascertain, in how many pints of air 4 pints of oxygen will be contained.

Now 100 parts of air by volume contain 21 parts of oxygen by volume. Therefore, if 21 pints of oxygen are contained in 100 pints of air, in how many pints of air will 4 pints of oxygen be contained?

$$21 : 4 :: 100 : x$$

x = 19·04 pints, the number of pints of air required for the combustion of 2 pints of marsh gas.

6. How many gallons of carbon monoxide are produced by passing 100 gallons of carbon dioxide over heated charcoal?

The equation representing the action of carbon dioxide on heated charcoal is first written out.

$$\underset{\text{2 molecules.}}{2CO_2} + 2C = \underset{\text{4 molecules.}}{4CO}$$

From this equation it is evident that 4 molecules of carbon monoxide are produced from 2 molecules of carbon dioxide, and therefore 4 gallons of carbon monoxide will be produced from 2 gallons of carbon dioxide.

4 gallons of CO are produced from 2 gallons of CO_2
∴ 2 ,, ,, ,, 1 ,, ,,
∴ 200 ,, ,, ,, 100 ,, ,,

7. How many pints of chlorine are required to convert 10 pints of marsh gas (methane) into chloroform?

The equation representing the conversion of marsh gas into chloroform by the action of chlorine is first written out.

$$\underset{\text{1 molecule.}}{CH_4} + \underset{\text{3 molecules.}}{3Cl_2} = CHCl_3 + 3HCl$$

From this equation it is evident that 3 molecules of chlorine are required to convert 1 molecule of marsh gas into chloroform, and therefore 3 pints of chlorine are required to convert 1 pint of marsh gas into chloroform. Therefore 30 pints of chlorine are required to convert 10 pints of marsh gas into chloroform.

WEIGHTS AND MEASURES.

1 lb. Avoirdupois... ... = 16 oz. Av.
,, ,, ... = 7,000 grains.
1 oz. Avoirdupois... ... = 437·5 grains.
1 lb. Troy ... ... = 12 ozs. Troy.
,, ,, ... = 5,760 grains.
1 oz. Troy ... ... = 480 grains.
1 gallon ... ... = 8 pints.
1 pint ... ... = 20 fluid ozs.
1 fluid oz. ... ... = 8 fluid drachms.
1 fluid drachm ... ... = 60 minims.
1 gallon of water at 62° F. weighs ... ... = 70,000 grains, or 10 lbs.
1 cubic foot of water ... = 997 ounces Av.

1 metre (m.) ... ... = 10 decimetres (dm.).
,, ,, ... = 100 centimetres (cm.).
,, ,, ... = 1,000 millimetres (mm.).
,, ,, ... = 39·37 inches.
1 litre ... ... = 1,000 cubic centimetres (c.c
,, ... = 1·76 pints.
1 cubic metre ... ... = 1,000 litres.
1 pint ... ... = 568 cubic centimetres.
1 fluid oz. ... ... = 28·4 ,, ,,
1 kilogramme (kg.) ... = 1,000 grammes (g.).
,, ,, ,, ... = 2·205 lbs. Av.
1 gramme ... ... = 10 decigrammes (dg.).
,, ... = 100 centigrammes (cg.).
,, ... = 1,000 milligrammes (mg.).
,, ... = 15·432 grains.
1 lb. Avoirdupois ... ... = 453·6 grammes.
1 oz. ,, ... = 28·35 ,,
1 grain .. .. = 64·8 milligrammes.

DIRECTIONS FOR EXAMINING A SALT OR SOLUTION CONTAINING NOT MORE THAN ONE METAL AND ONE ACID, OR ONE OF THE SUBSTANCES, CANE SUGAR, GRAPE SUGAR, OR UREA.

Examination of the Solution, or of the Salt dissolved in water or in hydrochloric acid (afterwards diluted with water), for Metals.

GROUP I.

To the Solution add HCl. If a p.p. occurs, see if it is soluble in excess of cold strong HCl; if it is soluble, proceed to Group II., as it will be Bi or Sb; if it is insoluble, add to the p.p. NH_4HO in excess.

SOLUBLE.	BLAOKENS.	UNAFFECTED.
Ag. Confirm by KHO to orig. *Brown p.p.* KI = pale yellow K_2CrO_4 to orig. *Red p.p.* Sol in HNO_3	Hg (-ous). Confirm by KHO to orig. *Black p.p.* KI to orig. *Dull Green p.p.*	Pb. Confirm by KI to orig. *Yellow p.p.* H_2SO_4 to orig. *White p.p.*

> Sb Group [illegible] Sol in excess of HCl.

GROUP II.

If no p.p. with HCl, fill a test tube half full with H_2S water and add a little of the liquid from Group I.

BLACK P.P.				YELLOW P.P.			ORANGE P.P.	BROWN P.P.
Add KHO to orig.				Collect p.p. on filter, wash, transfer to test tube and boil with equal parts of NH_4HO and NH_4HS.			Sb. Confirm by Reinsch's Cu test with orig.; also solution gives a black stain on Pt foil when in contact with a piece of Zn.	Sn (-ous). Confirm by $HgCl_2$ to orig. *White or grey p.p.*
No p.p. or Soluble in excess.	*Yellow p.p.*	*Blue p.p.*	*White p.p.*	*Insoluble.*	*Soluble.* Add KHO to orig.			
Pb. Confirm as in Group I.	Hg (-ic). Confirm by KI to orig. *Red p.p.* Cu sublimation test with orig. See mercury (test iv.), p.260.	Cu. Confirm by NH_4HO to orig. *Dark Blue colour.* $K_4Fe\,Cy_6$ to orig. *Red-brown p.p.*	Bi. Confirm by pouring a little of the HCl solution into water *White turbidity.*	Cd.	*White p.p.* Sn (-ic). Fuse on charcoal with KCN and Na_2CO_3 malleable bead of Tin. No incrustation.	*No p.p.* As. Confirm by Reinsch's Cu test with orig.		

NOTE.—The metals Cd and Sn (-ic and -ous) are not included in the syllabus of the Conjoint Board.

GROUP III.

If no p.p. with H_2S, *take a fresh portion* of the original Solution, add some Ammonium chloride and then Ammonium hydrate till the mixture smells (after mixing) of Ammonia.

A WHITE GELATINOUS P.P.	GREENISH P.P.	GREENISH P.P. (soon turning rusty brown on surface).	RUSTY BROWN P.P.
Al.	Cr.	Fe (-ous).	Fe (-ic).
p.p. soluble in KHO.	Borax bead.	HCl and K_3FeCy_6 to orig.	HCl and K_3FeCy_6 to orig.
Solid heated on charcoal, glows, when moistened with $Co(NO_3)_2$, and reheated gives	*Emerald Green.*	*Dark Blue p.p.*	*Dark Brown or Green colour.*
			HCl and K_4FeCy_6.
Bright Blue mass.			*Dark Blue p.p.*

NOTE 1.—Cr is not included in the Conjoint Board syllabus.

NOTE 2.—The ammonium chloride is added to prevent the pption. of Zn and Mg salts by the AmHO.

GROUP IV.

If no p.p. with AmHO and AmCl, add to the same Solution a little Ammonium sulphide.

WHITE P.P.	SALMON-COLORED P.P.	BLACK P.P.	
Zn. Heat solid on charcoal, Residue glows, s yellow when hot, white on cooling, if moistened with $Co(NO_3)_2$ and reheated. *Bright Green mass.*	Mn. Borax bead *Amethyst.* Fuse solid on Pt foil with KNO_3. Green manganate formed.	Co. Borax bead *Bright Blue.*	Ni. Borax bead *Sherry Red or Smoke colour.*

NOTE.—Zinc is the only metal in this group included in the Conjoint syllabus.

GROUP V.

If no p.p. in Group IV., add to same Solution $(NH_4)_2CO_3$, p.p. = Ca, Sr or Ba.
If a p.p. falls, add to orig. $CaSO_4$ Solution.

Immediate White p.p.	White p.p. forms on Standing for some time.	No p.p. on Standing.
Ba. Flame reaction. *Yellowish Green colour.*	Sr. Confirm by flame reaction. *Crimson colour.*	Ca. Confirm by NH_4HO and $(NH_4)_2C_2O_4$ to orig. *White p.p.*, insol. in $HC_2H_3O_2$. Sol. in HCl. *Flame colour, Orange Red.*

Note.—Sr is omitted in the Conjoint syllabus.

GROUP VI.

If no p.p. in preceding groups, treat fresh portions of orig. sol. successively as follows :—

Add NH_4Cl, NH_4HO in excess, and Na_2HPO_4.	Add KHO and boil.	Add HCl, $PtCl_4$ and stir.	Dip a platinum wire in the orig. and insert in Bunsen flame.	
White granular p.p.	*Odour of Ammonia.*	*Yellow granular p.p.*	*Yellow flame.*	*Crimson flame.*
Mg.	NH_4.	K.	Na.	Li.
Heat solid on charcoal, residue glows, on moistening with $Co(NO_3)_2$ and reheating.	*Gas* turns red litmus blue.	Confirm by stirring orig. with strong sol. of tartaric acid.		
Faint Pink mass.		*White granular p.p.*		
		Confirm by flame reaction.		
		Lavender tint.		

NOTE.—Li is not included in the Conjoint syllabus.

If no base is found the solution (1) either contains cane sugar, grape sugar, urea, or (2) is a solution of a free acid (HCl, HNO_3, H_2SO_4, $HC_2H_3O_2$, $H_2C_2O_4$, $HC_4H_4O_6$, HCN, etc.). Test the solution with blue litmus paper. If the solution is strongly acid and causes a vigorous effervescence with sodium carbonate, it contains a free acid, the nature of which is determined by the usual tests for acids (*see* below).

If, on the contrary, the solution is neutral, or nearly so, taste it: a sweet taste indicates one of the sugars. Apply the following tests:

Glucose (H_2SO_4 from Burnt Sugar)

$H_{12}O_6$ *Grape Sugar.*—Place in a test tube a small quantity of solution of copper sulphate, then add the solution, and finally, drop by drop, caustic potash until the solution becomes clear and dark blue. Heat gently; the blue colour disappears, a yellow p.p., turning red, falls. This indicates *grape sugar.* Reduces Fehling's Soln.

Cane Sugar.—(Sucrose)

$H_{22}O_{11}$

(1) The solution treated as above does not reduce the copper test; "Fehling's" is not reduced [illegible]

(2) Boiled with strong hydrochloric acid the original solution turns red, and finally becomes brown and thick;

(3) Boiled with strong sulphuric acid the solution ~~rapidly chars.~~ [illegible]

Urea.—

$O(NH_2)_2$

(1) NaBrO solution causes brisk effervescence owing to the escape of nitrogen;

(2) $Hg(NO_3)_2$, white p.p.;

(3) Strong HNO_3, if stirred in the cold with a *strong* solution of urea, gives white crystalline plates of urea nitrate.

H_2SO_4 no blackening

NH_4 evolved with heating

EXAMINATION FOR AN ACID.

TABLE I.

To original solid (or solution) add dil. HCl and warm; notice if any gas or odour is evolved.

Odourless Gas (with effervescence).	Odour of Rotten Eggs.	Odour of Burning Sulphur.		Odour of Hydrocyanic Acid.	Odour of Acetic Acid.	White Jelly Forms.
		Sol. remains clear.	Sol. becomes turbid.			
Carbonate or *Bicarbonate.*	*Sulphide.*	*Sulphite.*	*Hyposulphite.*	*Cyanide.*	*Acetate.*	*Silicate.*
Prove that the gas is CO_2 by its turning lime-water turbid.	Confirm by the gas blackening paper moistened with lead acetate.	Confirm by treating orig. with Zn and HCl, when H_2S should be evolved.	Confirm by adding $AgNO_3$, in excess, to orig.	Confirm by adding to orig. the following reagents in the order mentioned—KHO, $FeSO_4$, $FeCl_3$, and then, after heating, HCl.	Confirm by adding to orig. alcohol and H_2SO_4 and warming.	
			White p.p. changing to yellow, orange, brown, and black.	*Dark blue p.p. of Prussian blue formed.*	*Odour of Acetic Ether.*	

NOTE.—Sulphites, hyposulphites (or thiosulphates), and silicates are omitted from the syllabus of the Conjoint Board.

TABLE II.

Boil a little solid or a small quantity of the solution with excess of strong sulphuric acid.

Colourless fuming vapours of HCl.	Brown choking fumes of Br.	Brownish Red fumes of Oxides of Nitrogen.	Violet vapours of Iodine.	Chars, evolves SO_2 and odour of burnt sugar.	Effervesces when hot. CO and CO_2 evolved.	Odour of strong Vinegar.	Yellow gas, with Cl-like smell, which detonates on heating.
Chloride.	*Bromide.*	*Nitrate.*	*Iodide.*	*Tartrate.*	*Oxalate.*	*Acetate.*	*Chlorate.*
Confirm by reheating after adding a little MnO_2. *Chlorine* evolved which bleaches. Orig. solution with HNO_3 and $AgNO_3$ gives a white p.p. easily soluble in AmHO	Orig. solution with HNO_3 and $AgNO_3$. White p.p. soluble in excess of AmHO. Solution with Cl water and little $CHCl_3$, gives a *brown* solution of Br in $CHCl_3$.	Red fumes; more abundant by repeating the experiment with Cu turnings. Confirm by *brown ring* test. Mix cold orig. solution with its own vol. of strong H_2SO_4. Cool. Pour on $FeSO_4$ solution. Brown ring at junction of fluids.	Orig. solution with HNO_3 and $AgNO_3$. Yellowish p.p. insol. in AmHO. Solution with Cl water and little $CHCl_3$ gives *violet*-coloured solution of I. in $CHCl_8$.	Stir orig. solution with K_2SO_4 or KCl solution. White cryst. p.p. Confirm by the mirror test, *see* tartaric acid, p. 445. Citrate	CO burns with blue flame. Orig. solution with $HC_2H_3O_2$ and $CaCl_2$. White p.p.	Confirm as in Table I.	

NOTE.—Chlorates are omitted in the Conjoint syllabus.

TABLE III.

If no indication of the acid has been observed at this stage of the analysis, the probability is that the salt is a sulphate, phosphate (or perhaps a weak solution of an oxalate), or borate.

SULPHATE.	PHOSPHATE.	OXALATE.	BORATE.
To original solution add HCl and $Ba(NO_3)_2$. White p.p. = Sulphate.	To a small quantity of the original solution add strong HNO_3 and Am_2MoO_4 and boil. Yell. cryst. p.p. = Phosphate. Confirm by adding to original solution AmCl, AmHO and $MgSO_4$ and stirring. White cryst. p.p.	To original solution add $HC_2H_3O_2$ and $CaCl_2$. White p.p. = Oxalate.	1. Acidify original solution with HCl; dip into this solution a piece of turmeric paper: on drying, the paper turns reddish; the red colour becomes dark blue on adding ammonia. 2. Mix original substance with strong sulphuric acid and excess of alcohol in a dish and set the mixture on fire. The alcohol burns with a green-edged flame.

NOTE.—Borates are omitted in the Conjoint syllabus.

If arsenic has been found when testing for the base, special tests must be made to determine whether this element is present as a base, probably as $AsCl_3$, or as an acid combined with potash or soda, as arsenite or arseniate. An arsenite gives with $AgNO_3$ a yellow p.p., an arseniate with $AgNO_3$ gives a red p.p.

The solution of a chromate is yellow and gives a red p.p. with $AgNO_3$. The yellow colour is turned dark green by reducing agents, such as SO_2, H_2S, nascent hydrogen, etc.

COMMON COLOURED SUBSTANCES.

Red. Pb_3O_4, HgS, HgO, HgI_2, Fe_2O_3, Sb_2S_3, Cu_2O.

Yellow. Ferric salts, PbO, PbI_2, HgO (ppted.), As_2S_3, S.

Brown. Fe_2G_3, PbO_2.

Green. Copper salts, ferrous salts.

Blue. Copper salts.

Black. PbS, FeS, Bi_2S_3, HgS, CuS, CuO, MnO_2, C, finely divided metals.

ADDITIONAL HINTS.

I. If the original solution is strongly alkaline, and carbonates are absent, the presence of a soluble base, such as ammonia, potash, soda, lime, or baryta is indicated. Ammonia would be detected by its smell, the other bases by a brown p.p. on addition of $AgNO_3$.

II. If the salt is insoluble in boiling water, attempts should be made to dissolve it in HCl. If it dissolves without effervescence, the absence of a carbonate is indicated. To prove an oxide, since the metal has been previously detected, the physical and chemical properties of the oxide of that metal must be borne in mind, and searched for; a few oxides, such as oxide of mercury, black oxide of manganese, and peroxide of lead, evolve oxygen on heating; litharge is of a characteristic yellow colour; oxide of bismuth of a lemon colour; oxide of copper black, forming with acids a green solution; oxide of antimony a buff colour, dissolving when boiled with tartaric acid solution; ferric oxide a reddish-brown colour; oxide of zinc a white colour, turning yellow when heated, but becoming white again on cooling.

III. The following are some of the reactions by which some of the more commonly occurring bodies, insoluble in HCl, may be recognised :—

Calomel, by its turning black when treated with alkalies, and by its volatility. If treated with AmHO and filtered, the Cl can be detected in the filtrate by acidifying with HNO_3 and adding $AgNO_3$. If heated in a small tube with dry sodium carbonate metallic mercury sublimes.

Mercuric Iodide, by its scarlet colour, and by its turning yellow on heating and scarlet again when the yellow modification is pressed.

Mercurous Iodide, by its dirty-green colour, and by its yielding some yellow and scarlet mercuric iodide when heated in a dry tube.

Mercurous Oxide, by its black colour, by its evolving oxygen, and by its yielding a sublimate of metallic mercury on heating.

Oxide of Silver, by its brown colour, and by its evolving oxygen when heated, the metal silver being left.

Sulphur, by its yellow colour, and by the peculiar odour of SO_2 when burnt.

Charcoal, by its black colour, by its deflagrating when heated with KNO_3, and by its evolving SO_2 when boiled with strong H_2SO_4.

In many cases, although a substance is not, strictly speaking, insoluble, it is so difficult to dissolve and so much acid is usually employed by the student, that ordinary analytical reactions are somewhat obscured. Thus, some specimens of litharge and other oxides of lead are very difficult to dissolve; in such cases **a preliminary examination** by the blowpipe, or in the dry way, is often *most useful*. This consists of four principal experiments:—(1) heating in a small glass tube; (2) heating on charcoal; (3) borax bead; (4) flame coloration. The principal reactions are as follows:

(1) Heat solid in small glass tube—

1. Substance sublimes indicates As, Hg, Am salts, etc.
   Heat with Na_2CO_3, sublimate of silvery
   globules . . . . = Hg.
   garlic odour and black mirror . = As.
   NH_3 evolved . = NH_4 salts.
2. Substance chars = Sugar, tartrates, etc.
3. Substance turns yellow when hot, white on cooling = Zn salts.
4. Gases evolved, brown = Nitrate or bromide.
   ,, ,, violet = Iodide.

(2) Heat solid on charcoal—

1. Substance deflagrates = Nitrate or chlorate.
2. Residue glows = Zn, Al, Mg salts.
   Residue moistened with $Co(NO_3)_2$ and reheated:
   (*a*) green mass = Zn.
   (*b*) blue mass = Al.
   (*c*) faint pink = Mg.
3. A metallic globule is formed. (The formation of these globules is aided by the addition of a little dry Na_2CO_3 before heating.)

(*a*) White malleable, no incrustation = Ag or Sn.
(*b*) " " yellow " = Pb.
(*c*) " brittle, orange " = Bi.
(*d*) " " white " = Sb.
(*e*) Red scales . . . . = Cu.

(3) Borax bead—

1. Green in both flames . . . . = Cr.
2. { In outer flame, green when hot, blue cold / In inner flame, red streaks . . . } = Cu.
3. Blue in both flames . . . . = Co.
4. In outer flame violet, in inner colourless = Mn.
5. { In outer flame, brown-yellow, lighter on cooling; in inner flame, olive green } = Fe.
6. Smoke coloured, or sherry red . . = Ni.

(4) Flame coloration—

1. Crimson = Sr or Li.
2. Orange red = Ca.
3. Green = Cu, Ba, or boric acid.
4. Lavender = K.
5. Livid blue = As, Sb, Pb.
6. Orange yellow = Na.

PREPARATION OF CERTAIN TYPICAL SALTS.

Sodium Chloride.—Dissolve 20 grammes of ordinary washing soda in about 100 c.c. of water contained in an evaporating dish, add hydrochloric acid until the mixture, on stirring and boiling, is *quite neutral*, *i.e.* does not change the colour of either blue or red litmus paper. (The litmus paper should not be dipped into the solution, but, after vigorous stirring, a small drop should be taken up on a glass stirring-rod and brought into contact with the litmus paper.) As salt is almost as soluble in cold as in hot water, the solution must, after filtering if necessary, be evaporated to dryness to obtain the sodium chloride.

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O.$$

Ammonium Chloride.—Take about 30 c.c. of strong hydrochloric acid, dilute and neutralise by adding ammonium hydrate. Test the solution with litmus, as above. When neutral, evaporate to a small bulk and allow to cool. Drain the crystals on several thicknesses of filter paper.

$$NH_4HO + HCl = NH_4Cl + H_2O.$$

Lead Chloride.—Dissolve 5 grammes of lead acetate or lead nitrate in distilled water, add dilute hydrochloric acid as long as a precipitate falls. Filter off the precipitate and wash with a little water. The precipitate may be dissolved by boiling in distilled water, and on cooling the lead chloride will be obtained in crystals.

$$Pb(NO_3)_2 + 2HCl = PbCl_2 + 2HNO_3.$$

Lead Iodide.—Dissolve 5 grammes of lead acetate or nitrate in distilled water, adding a little nitric acid; then add a solution of potassium iodide as long as a precipitate falls. Filter, wash with cold distilled water, and dry on filter paper. If the precipitate be boiled with distilled water containing a little nitric acid, and the solution be allowed to cool, the lead iodide will separate out in iridescent golden spangles.

$$Pb(C_2H_3O_2)_2 + 2KI = PbI_2 + 2KC_2H_3O_2.$$

Mercuric Iodide.—Dissolve 5 grammes of corrosive sublimate in water; add solution of potassium iodide as long as a precipitate falls (avoid excess of potassium iodide, as mercuric iodide is soluble in excess). Filter, wash, and dry.

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

Cupric Oxide (*Black Oxide of Copper*).—Dissolve 5 grammes of copper sulphate in water; precipitate with caustic potash. Boil the mixture, with constant stirring, until the blue precipitate ($Cu(HO)_2$) becomes black (CuO). Filter, wash well, and dry.

$$CuSO_4 + 2KHO = Cu(HO)_2 + K_2SO_4.$$

$$Cu(HO)_2 = CuO + H_2O.$$

Cupric Hydrate.—Dissolve 5 grammes of copper sulphate in water; precipitate carefully *in the cold* with caustic potash. Avoid excess of caustic potash. Filter, wash, dry on filter paper, *without heat.*

Mercuric Oxide (*Red Oxide of Mercury*).—Dissolve 25 grammes or 2 c.c. of mercury in an evaporating dish, in strong nitric acid (this must be performed in a draught cupboard). Evaporate the solution to dryness. As soon as the liquid has all evaporated, remove the white crystalline cake of mercuric nitrate and powder it in a mortar. Replace the powder in the dish, and heat, with constant stirring, until its colour is uniformly dark and red fumes cease to be evolved. Allow it to cool; when cold, it will be bright red.

$$3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 2NO + 4H_2O.$$

$$Hg(NO_3)_2 = HgO + 2NO_2 + O.$$

Mercuric Oxide (*Yellow Oxide of Mercury*).—Dissolve 5 grammes of mercuric chloride in distilled water and precipitate with caustic potash. Filter, wash and dry.

$$HgCl_2 + 2KHO = HgO + H_2O + 2KCl.$$

Sodium Hydrate (*Sodium Hydroxide or Caustic Soda*).—Dissolve 20 grammes of washing soda in water in an evaporating dish; add about 20 grammes of freshly-made lime. Boil the mixture, with occasional stirring, for ten minutes, *filling up the dish with water as it boils away.* Decant or filter, and evaporate the clear liquid until there remains in the dish a thick, almost viscid, liquid. Allow it to cool, when it should solidify into a mass of caustic soda, which should not effervesce when dilute hydrochloric acid is poured over it.

$$Na_2CO_3 + Ca(HO)_2 = 2NaHO + CaCO_3.$$

Sodium Carbonate.—Dissolve 5 grammes of caustic soda in water in a flask. Bubble carbon dioxide through the solution till a portion of the solution ceases to give a brown precipitate with silver nitrate. Filter if necessary, and evaporate the clear solution till a drop taken out on the end of a glass stirring-rod and allowed to cool shows signs of crystallisation; then allow the whole of the liquid to cool slowly. When cold, pour off the mother liquor and allow the crystals to drain.

$$2NaHO + CO_2 = Na_2CO_3 + H_2O.$$

Calcium Carbonate.—Dissolve 10 grammes of lime or whiting in dilute hydrochloric acid, with the aid of heat. Add ammonium hydrate to the solution till alkaline. Filter off the precipitate (containing usually calcium phosphate, aluminium oxide and iron oxide) and add to the clear liquid ammonium carbonate as long as a precipitate falls. Boil, filter, wash and dry.

$$Ca(HO)_2 + 2HCl = CaCl_2 + 2H_2O;$$

$$\text{Or, } CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$

$$CaCl_2 + Am_2CO_3 = CaCO_3 + 2AmCl.$$

Magnesium Carbonate.—Dissolve 5 grammes of magnesium sulphate in water; precipitate with sodium carbonate. Boil, filter, wash, and dry.

$$MgSO_4 + Na_2CO_3 = MgCO_3 + Na_2SO_4.$$

The normal $MgCO_3$ is not usually obtained, but a basic carbonate,

$$3MgCO_3 + Mg(HO)_2 + 4H_2O.$$

Bismuth Carbonate.—Dissolve 3 grammes of bismuth nitrate in distilled water in a flask. Boil, add nitric acid drop by drop, with constant shaking, until a clear solution is obtained; cool, and add ammonium carbonate solution in excess; filter, wash, and dry.

$$2Bi(NO_3)_3 + 3Am_2CO_3 = Bi_2(CO_3)_3 + 6AmNO_3.$$

As with magnesium, the normal carbonate is not usually formed, the precipitate having the composition

$$2(BiO)_2CO_3 + H_2O.$$

Ammonium Oxalate.—Dissolve 5 grammes of oxalic acid in distilled water; carefully neutralise with ammonium hydrate, evaporate to the crystallising point (*see* Sodium Carbonate, page 520), and allow to cool.

$$H_2C_2O_4 + 2AmHO = Am_2C_2O_4 + 2H_2O.$$

Urea Oxalate.—Dissolve 4 grammes of oxalic acid in 40 c.c. of distilled water; dissolve 2 grammes of urea in 2 c.c. of distilled water; add about 30 c.c. of the cold oxalic acid solution to the solution of urea, and mix by gently shaking in a flask. Allow to stand for a short time, filter off the crystals, wash with a little distilled water and dry on filter paper.

$$2CO(NH_2)_2 + H_2C_2O_4 = (CO(NH_2)_2)_2.H_2C_2O_4.$$

Potassium Nitrate.—Dissolve 10 grammes of caustic potash or of potassium carbonate in water; neutralise with nitric acid, evaporate to the crystallising point, and allow to cool.

$$K_2CO_3 + 2HNO_3 = 2KNO_3 + CO_2 + H_2O.$$

Barium Nitrate.—Dissolve 10 grammes of barium carbonate in *dilute* nitric acid with the aid of heat, boil, filter hot, evaporate to the point of crystallisation and allow to cool. It is most important to have the solution *dilute* and *hot* while filtering, as barium nitrate is not very soluble: if the solution is strong, most of the barium nitrate will separate out and remain on the filter.

$$BaCO_3 + 2HNO_3 = Ba(NO_3)_2 + CO_2 + H_2O.$$

Lead Nitrate.—Dissolve 10 grammes of lead carbonate or of litharge in dilute nitric acid, with the aid of heat; filter the solution, evaporate to the point of crystallisation, and allow to cool.

$$PbCO_3 + 2HNO_3 = Pb(NO_3)_2 + CO_2 + H_2O.$$

Calcium Phosphate.—Dissolve 10 grammes of whiting in dilute hydrochloric acid; boil, add ammonium hydrate till alkaline; filter, if necessary, add to the clear filtrate sodium phosphate as long as a precipitate falls; filter, wash, and dry the precipitate.

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$

$$3CaCl_2 + 2HNa_2PO_4 + 2AmHO = Ca_3(PO_4)_2 + 4NaCl$$

$$+ 2AmCl + 2H_2O.$$

Ferrous Phosphate.—Dissolve 10 grammes of ferrous sulphate in water with a few drops of dilute sulphuric acid; dissolve 3 grammes of sodium acetate in hot water and add the solution to the ferrous sulphate. Boil, and precipitate with sodium phosphate; filter the precipitate, wash, and dry.

$$3FeSO_4 + 2HNa_2PO_4 + 2NaC_2H_3O_2 = Fe_3(PO_4)_2 +$$

$$3Na_2SO_4 + 2HC_2H_3O_2.$$

Sodium Sulphate.—Dissolve 10 grammes of washing soda in water; add dilute sulphuric acid till the solution is neutral to litmus paper; filter, if necessary; evaporate the filtrate to the crystallising point and allow to cool.

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O.$$

Calcium Sulphate.—Dissolve 10 grammes of whiting in dilute hydrochloric acid; filter, if necessary, add dilute sulphuric acid to the filtrate as long as a precipitate falls, filter off the precipitate, wash with a little water; dry.

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$

$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl.$$

Magnesium Sulphate.—Dissolve 18 grammes of magnesium carbonate in dilute sulphuric acid; add 2 grammes of magnesium carbonate; boil and filter. Evaporate the filtrate to the crystallising point; allow to cool.

$$MgCO_3 + H_2SO_4 = MgSO_4 + CO_2 + H_2O.$$

Zinc Sulphate.—Dissolve 5 grammes of zinc dust or 10 grammes of zinc oxide in dilute sulphuric acid, avoiding an excess of acid. Filter, evaporate the filtrate to the crystallising point, and allow to cool.

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O.$$

Copper Sulphate.—Dissolve (in a draught cupboard) 5 grammes of copper turnings in an evaporating dish, in strong sulphuric acid; the reaction must be aided by heat. When the metallic copper has been converted into a grey powder allow the mixture to cool. Cautiously pour off the excess of strong sulphuric acid and pour on the residue cold water; boil, filter, evaporate the filtrate to the crystallising point and allow to cool. The strong sulphuric acid converts the copper into the anhydrous copper sulphate (mixed with a little sulphide). This is insoluble in the strong acid; on adding water the grey powder dissolves to a blue solution of ordinary copper sulphate ($CuSO_4 + 5H_2O$).

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

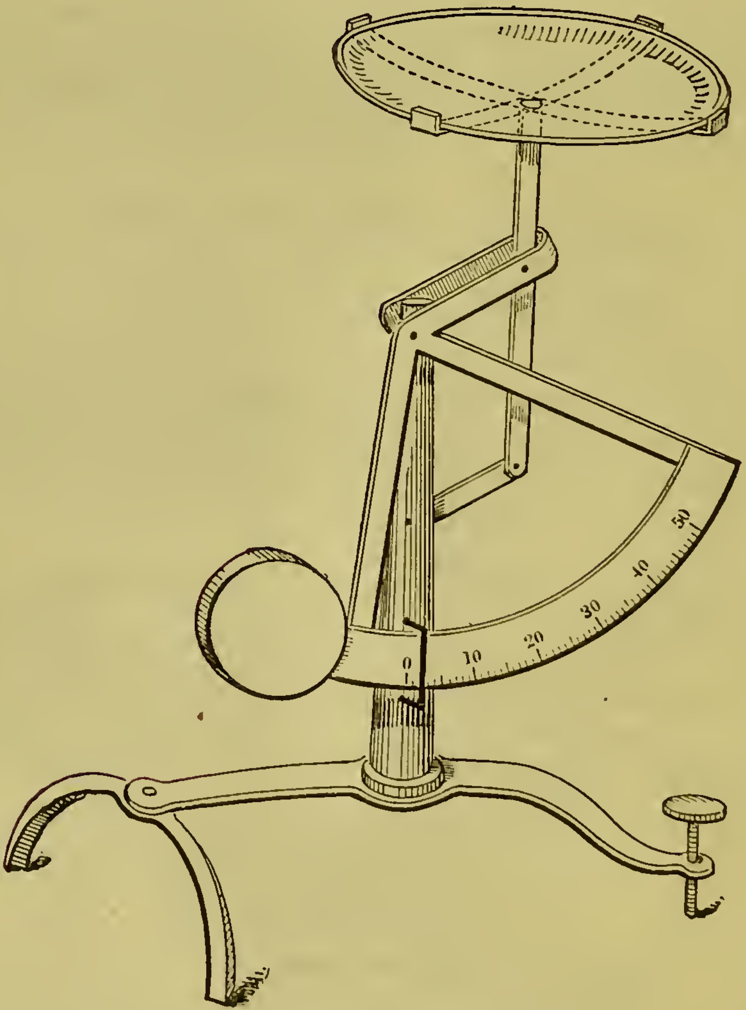


Fig. 40.—Gramme Letter Balance.

In making these preparations a little shilling letter-balance, graduated in grammes, and which has a detachable glass pan, is most useful. It can be obtained at most of the apparatus dealers.

APPENDIX

COVERING THE NEW SYNOPSES OF THE CONJOINT BOARD AND THE SOCIETY OF APOTHECARIES.

In the new regulations applicable to those commencing their studies on or after June 1st, 1904, the candidate is required—

I.—To perform the analysis of a simple salt, or a mixture of two metals and one acid, selected from a list which is the same as the list in the old synopsis except that

- (*a*) the metal Tin is added;
- (*b*) the acetates, oxalates, tartrates, and cyanides of *any* of the metals may be given.
- (*c*) Cane sugar, grape sugar, and Urea are omitted; the metallic substances may be present as element, oxide, sulphide, a simple salt or a mixture; the acids may be present in the free state, or as a simple salt.

II.—To prepare various compounds in a well crystallised condition; many of the old preparations are omitted, while Ferrous sulphate, Lead acetate, Acid potassium tartrate, and Tartar emetic are added.

III.—To estimate the strengths of solutions of Potassium or Sodium hydrates by standard sulphuric acid, and of dilute hydrochloric or nitric acids by standard sodium hydrate; also to estimate (the strength of) solutions of oxalic acid by standard potassium permanganate.

It will be seen that under the new regulations the Practical examination is a much more serious business than heretofore. It is true that candidates will be allowed the use of books or tables at the Practical examination, but the student is most strongly advised to *learn* his tables, etc., as if he does not know them he will probably lose much time by hunting about in the books for what he wants. The books, however, should be taken into the examination, as they may be useful if the student happens to forget the equations illustrating the chemical reactions involved in testing.

In the analysis of a mixture of two bases, if one of the metals is in the H_2S group the student *must* use H_2S *gas* to pp the metal; the use of a *solution* of H_2S which answers well enough with a simple salt is impracticable with a mixture, since, in order to effect complete precipitation, the volume of the fluid would be increased to such an extent that the subsequent filtrations could not be effected in the time allowed.

The principal difference between the analysis of a simple salt and a mixture of bases is, that in the latter the precipitates in the various groups are separated off by filtration, and the various precipitates tested as simple substances, remembering that each pp can only contain the metals belonging to that group. Thus, suppose a pp is obtained with Am_2CO_3, this pp is only tested for Ba (Sr) or Ca.

Another difference is that the *same* solution must be used from beginning to end; thus if a pp is obtained with H_2S this pp is filtered off and the filtrate (not a fresh solution) used for the rest of the groups; now as this filtrate is saturated with H_2S the latter must be boiled off, otherwise, on adding AmHO, Am_2S would be formed, and the third and fourth groups would come down together; in order to get rid of the H_2S the filtrate is boiled in a *dish* for some minutes, till free from that gas. Here another complication arises: iron when present as a ferrous salt is not completely precipitated by AmHO, so it must be converted into a ferric salt; this is effected by adding some strong HNO_3 and boiling for a few minutes.

Lastly, the testing for potassium in a mixture is much more troublesome than in a simple salt, the flame coloration is most misleading, as various Antimony, Arsenic, and Lead compounds give a very similar flame coloration, and the only safe way to test for potassium in a mixture is to evaporate the filtrate from the Am_2CO_3 group down to dryness in a dish, scrape the residue on to platinum foil, heat this till it is thoroughly red hot all over, to get rid of ammonium salts, then dissolve off the residue in a few drops of water, pour the solution into a watch glass, and stir with Platinum chloride and alcohol in the usual way.

TABLE FOR THE ANALYSIS OF A SUBSTANCE CONTAINING TWO BASES (TAKEN FROM THE CONJOINT LIST).

Dissolve the substance in water (or HCl or HNO_3); to the solution add—

HCl (if a pp occurs see that it is not soluble in excess of HCl before proceeding).

pp indicates Ag, Hg (ous), or Pb.

Filter off pp (keep the filtrate "A") and wash with a little water.

Treat the pp with AmHO.

pp dissolves = Ag, confirm as on p. 504.

pp turns black = Hg (ous), confirm as on p. 504.

pp unaltered = Pb, confirm as on p. 504.

Reactions: group pp.

$$AgNO_3 + HCl = AgCl + HNO_3$$

$$Hg_2(NO_3)_2 + 2HCl = \underset{\text{calomel}}{Hg_2Cl_2} + 2HNO_3$$

$$Pb(NO_3)_2 + 2HCl = PbCl_2 + 2HNO_3$$

Reaction of AmHO on mercurous chloride—

$$Hg_2Cl_2 + AmHO = 2AmCl + \underset{\text{black oxide}}{Hg_2O} + H_2O$$

Pass **H_2S** *gas* through filtrate "A," best placed in a small flask, till, after shaking, it smells strongly of the gas.

A black or brown pp = Pb, Hg (ic), Cu, Bi, or Sn (ous).

A yellow pp = As, or Sn (ic).

An orange pp = Sb.

Filter off the pp (keep the filtrate "B"), wash with a little water, and boil with KHO (if Sn is suspected add Am_2S) filter (keep filtrate 1); the residue, not dissolved by KHO, may be HgS, PbS, CuS, Bi_2S_3; boil this with a little strong HNO_3.

Residue (which settles at the bottom of the tube) is black = Hg (ic), confirm as on pp. 260 and 505.

Solution blue = Cu, add AmHO, a dark blue colour, confirm as on p. 505.

Solution colourless = Pb or Bi, apply the tests as on pp. 504 and 505.

Filtrate 1. Acidify with HCl.

White pp of sulphur can be neglected.

Yellow pp = SnS_2 or As_2S_3.

Orange pp = Sb_2S_3.

Filter off the pp and boil with strong HCl insoluble residue = As, confirm by bulb tube test, p. 285, and Reinsch test, p 286, solution of pp may contain Sb or Sn. Dilute the solution and pour into a dish with Zn and Pt foil.

A black stain on the platinum = Sb, confirm by Reinsch test, p. 294.

A spongy grey mass on the zinc = Sn, dissolve the zinc and tin completely in strong HCl, dilute and add $HgCl_2$; a white pp confirms Sn (p. 269).

Reactions: group pp.

$PbCl_2 + H_2S = PbS + 2HCl$

Same with Cu, Hg, and Sn(ous)

$3BiCl_3 + 3H_2S = Bi_2S_3 + 6HCl$

Same with As and Sb

Through filtrate B pass a little more H_2S to make sure that all the metals in the H_2S group are precipitated, place the filtrate in a dish and boil vigorously for three or four minutes to drive off the H_2S, then add a few drops of strong HNO_3 and boil; pour the liquid into a test tube and add—

AmCl and **AmHO** until the fluid *smells of* NH_3 *after mixing;* filter off pp, if any (keep filtrate C).

Rusty brown pp = Fe; the original solution must be tested, as on p. 506, to see if the iron is present as ferrous or ferric.

Colourless gelatinous pp, soluble in KHO = Al; filter off the pp, tear off the apex of the filter, and after dipping in dilute $Co(NO_3)_2$, ignite on Platinum foil; a blue mass confirms Al.

A white pp not soluble in KHO may be Calcium, Barium, or Magnesium oxalate or phosphate; test for the acid:

1. If an oxalate is found, filter off the pp

and ignite on platinum foil, this converts it into a carbonate (see bottom of p. 442) which can be dissolved in HCl, and the metal tested for as on pp 506-509.

ii. If a phosphate is found, a careful examination of the flame coloration, after moistening with strong HCl, will generally decide between Ca and Ba. See also note at the end of this table.

Reactions : Group pp

$$FeCl_3 + 3AmHO = Fe(HO)_3 + 3AmCl$$

Same with Al

To filtrate C add **Am_2S.**

White pp = Zn ; filter off the pp (keep filtrate D), scrape off the pp with a loop of platinum wire, moisten with dilute $Co(NO_3)_2$, and heat carefully in a Bunsen burner; a green residue on the wire confirms Zn.

Reaction : group pp

$$ZnCl_2 + Am_2S = ZnS + 2AmCl$$

[If the fluid turns green or gives a black pp with Am_2S, this indicates imperfect precipitation of the metals in the H_2S or AmHO group.]

To filtrate D add **Am_2CO_3.**

Pp = Ca or Ba ; filter off pp (keep filtrate E), wash with water and pour on the filter paper a little hot dilute HCl ; if necessary pour the liquid, which runs through, over the filter a second time, divide the solution into two parts—"a" and "b"; to "a" add $CaSO_4$ white pp = Ba, confirm by flame coloration (p. 508).

No pp with $CaSO_4$ = absence of Ba : to "b," add AmHO and $Am_2C_2O_4$ white pp = Ca, confirm by flame coloration.

Reaction : group pp

$$BaCl_2 + Am_2CO_3 = BaCO_3 + 2AmCl$$

Same with Ca

Confirmatory tests :

$$BaCl_2 + CaSO_4 = BaSO_4 + CaCl_2$$

$$CaCl_2 + Am_2C_2O_4 = CaC_2O_4 + 2AmCl$$

To a small portion of filtrate E add **HNa_2PO_4**, and rub the sides of the test tube with a glass rod.

White pp = Mg.

Reaction:

$$MgCl_2 + AmHO + HNa_2PO_4 = \underset{\text{White pp}}{MgNH_4PO_4} + 2\,AmCl$$

Evaporate the rest of filtrate E to dryness, scrape the residue on to platinum foil and make the latter red-hot all over. Shake the foil in a test tube with a *little* water until any residue on the foil is dissolved. Pour nearly all the solution into a watch glass and stir with **$PtCl_4$** and alcohol, a yellow cryst. pp = K; confirm, if possible, by flame coloration.

$$2KCl + PtCl_4 = K_2PtCl_6$$

No pp with $PtCl_4$ = absence of K.

The remainder of the solution gives an *intense* yellow flame coloration = Na.

Test the original substance for ammonium by boiling with **KHO**, or mixing the solid with a little solid lime and water. NH_3 gas is evolved, turning moist red litmus blue = Am.

$$NH_4Cl + KHO = NH_3 + KCl + H_2O.$$

Note 1.—If the pp in the AmHO group contains phosphoric acid it should be treated as follows:

Dissolve the pp in dilute HCl, nearly neutralise with Na_2CO_3 solution, add an excess of sodium acetate and a little acetic acid; $FeCl_3$ is then added till the fluid turns yellow, when the whole is boiled and filtered (in this way the phosphoric acid is precipitated as Ferric phosphate ($FePO_4$) and the excess of iron thrown down by boiling, as basic acetate). The filtrate is made alkaline by adding AmHO, and again filtered if necessary; the filtrate is tested for Ca, Ba, and Mg as usual.

Iron phosphate can be detected by the usual tests, using K_4FeCy_6 and K_3FeCy_6 for the iron.

Note 2.—If a tartrate is found, filtrate B should be evaporated quite to dryness with HNO_3, or the original substance ignited on platinum foil; since a tartrate prevents the precipitation of iron by AmHO, and the iron comes down as a black pp in the Am_2S group.

Note 3.—Insoluble substances as $BaSO_4$ should be fused on platinum foil with about three times their weight of Na_2CO_3, the fused mass extracted with water and filtered:

the filtrate contains the acid as a sodium salt, and the residue, insoluble in water, the metal, as carbonate, which can be dissolved in dilute HCl and tested for as usual.

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3$$

The same decomposition can be partially effected by boiling the $BaSO_4$ with a strong solution of Na_2CO_3.

PREPARATION OF CERTAIN TYPICAL SALTS.

Ferrous sulphate.—$FeSO_4 + 7H_2O$. Dissolve 5 grams of fine iron wire or reduced iron in dilute sulphuric acid, filter, evaporate, and crystallise; avoid exposure to the air as much as possible.

$$Fe + H_2SO_4 = FeSO_4 + H_2$$

Lead Acetate.—$Pb(C_2H_3O_2)_2 + 3H_2O$. Dissolve 5 grams of litharge or lead carbonate by boiling with acetic acid, filter, evaporate, and crystallise.

$$PbO + 2HC_2H_3O_2 = Pb(C_2H_3O_2)_2 + H_2O$$

Acid tartrate of potassium $HK(C_4H_4O_6)$.

a. Dissolve 5 grams of potassium chloride in a small quantity of water and 6 grams of tartaric acid also in a small quantity of water, mix the solutions and allow to stand; filter off the white pp, and recrystallise from boiling water.

$$2KCl + H_2C_4H_4O_6 = 2HKC_4H_4O_6$$

b. Dissolve 5 grams of tartaric acid in water, divide the solution into two equal parts, *neutralise* one carefully with KHO, then mix it with the rest of the tartaric acid, allow to stand, filter and recrystallise from hot water.

$$2KHO + H_2C_4H_4O_6 = K_2C_4H_4O_6 + H_2O$$
$$K_2C_4H_4O_6 + H_2C_4H_4O_6 = 2HKC_4H_4O_6$$

Tartar emetic. $2KSbOC_4H_4O_6 + H_2O$. Boil 5 grams of antimony oxide, 7 grams of cream of tartar, and 40cc of water for ten minutes, filter through a funnel and filter paper, previously warmed by pouring through them boiling water, and allow to crystallise.

$$Sb_2O_3 + 2HKC_4H_4O_6 = 2KSbOC_4H_4O_6$$

VOLUMETRIC ANALYSIS.

Volumetric analysis is so called because the quantity of a substance is estimated by *measuring* a certain *volume* of a liquid, as contrasted with gravimetric analysis in which the substance is precipitated, filtered, washed, dried, and *weighed.*

Thus, suppose the amount of chlorine in a solution of salt is to be determined—

By the gravimetric method an excess of silver nitrate solution is added to a known volume of the solution of salt, all the chlorine is thrown down as silver chloride, this is filtered off, washed till free from silver nitrate, dried, the filter paper burnt off, and the silver chloride weighed. This procedure obviously takes a considerable time and requires a delicate balance.

By the volumetric method a solution of silver nitrate, of which the strength is accurately known, called the *standard* solution, is added from a graduated vessel to a known volume of the salt solution contained in a stoppered bottle, a precipitate of silver chloride is formed, which is well shaken and allowed to settle, more standard solution is added, and so on until the last addition of silver nitrate gives no precipitate; if we know the volume of standard solution used, and its strength, we can estimate the chlorine in about as many minutes as the gravimetric process takes hours.

Suppose, for example, the standard silver nitrate solution was of such a strength that one cubic centimetre would precipitate exactly 1 centigram (·01 grm.) of Cl.

50cc. of salt solution required 40cc. of standard silver nitrate solution to precipitate all the Cl.

As 1cc. = 0·01 gram of Cl

40cc. = 0·4 gram of Cl in 50cc. of the salt solution, or ·65 gram of sodium chloride.

The standard solution can be made of any strength, but a *certain* strength is found to be particularly convenient for ordinary work; this is the *normal* solution.

A normal solution contains the hydrogen equivalent of the active substance in grams per litre or 1,000cc.

Thus normal HCl, usually written $\frac{N}{1}$HCl, contains

$1 + 35{\cdot}5 = 36{\cdot}5$ grams of HCl per litre.

$\frac{N}{1}HNO_3$ $1 + 14 + 48 = 63$ grams of HNO_3 per litre.

$\frac{N}{1}H_2C_2O_4 + 2H_2O$ $\frac{2 + 24 + 64 + 36}{2} = 63$ grams of oxalic acid per litre.

$\frac{N}{1}H_2SO_4$ $\frac{2 + 32 + 64}{2} = 49$ grams of H_2SO_4 per litre;

it will be noticed that the molecular weights of the dibasic acids, oxalic and sulphuric, are divided by 2 so as to obtain the weights which contain one of replaceable hydrogen.

$\frac{N}{1}NaHO$ $23 + 1 + 16 = 40$ grams of $NaHO$ per litre.

$\frac{N}{1}KHO$ $39 + 1 + 16 = 56$ grams of KHO per litre.

$\frac{N}{1}Ba(HO)_2$ $\frac{137 + 2 + 32}{2} = 85{\cdot}5$ grams of $Ba(HO)_2$ per litre.

Very often the normal solution is too strong and $\frac{N}{10}$ a decinormal, or $\frac{N}{100}$ centinormal, solution is employed instead.

The great advantage of normal solutions of acids and alkalies is that a litre of any or all of them has exactly the same neutralising power, thus—

$$NaHO + HCl = NaCl + H_2O$$
$$KHO + HCl = KCl + H_2O$$

i.e. 40 grams of $NaHO$ neutralise the same weight of HCl as 56 grams of KHO, and these are the respective quantities contained in a litre of $\frac{N}{1}NaHO$ and $\frac{N}{1}KHO$, so that a litre of normal soda neutralises the same quantity of acid as a litre of normal potash.

The same holds good with the acids thus—

$$NaHO + HCl = NaCl + H_2O$$
$$2NaHO + H_2SO_4 = Na_2SO_4 + 2H_2O$$

i.e. 36·5 grams of HCl neutralise 40 grams of $NaHO$, and 98 grams of H_2SO_4 neutralise 80 grams of $NaHO$, or 49 grams of H_2SO_4 neutralise 40 grams of $NaHO$. So a litre of $\frac{N}{1}H_2SO_4$ neutralises the same weight of $NaHO$ as a litre of $\frac{N}{1}HCl$.

In order to make accurate determinations by volumetric analysis there are required three essentials :

1. Accurately graduated vessels.

2. Accurate standard solutions, which must not be too strong.

3. The change which denotes the end of the reaction must be sharp and easily recognised by the eye.

The various volumetric processes may be divided into three main groups.

1. Those in which one substance neutralises another of opposite properties, as when an acid is added to a base, or a base to an acid.
2. Those in which a reducing or oxidising agent of known strength is used.

   Reducing agents: Solutions of ferrous salts, oxalic acid, sodium thiosulphate, etc.

   Oxidising agents: Potassium permanganate, Potassium bichromate, Iodine, etc.
3. Those in which the standard solution precipitates the substance to be analysed, as silver by solution of salt.

The fluid to be analysed is conveniently measured in a pipette or a measuring flask; the standard solution is delivered from a vertical glass tube of uniform bore called a "burette," which usually contains 50 cc. and is graduated into $\frac{1}{10}$ of a cc.; it is furnished at its lower end with some kind of tap. The *lower* meniscus of the fluid surface is usually read, and the eye must be *level* with the meniscus when reading. The burette, after thorough washing with distilled water, should always be rinsed out with a small quantity of the standard solution, and the air bubble in the tap washed out before reading; the graduation at which the meniscus stands *should always be written down* before commencing the analysis.

VARIOUS TYPICAL ESTIMATIONS.

1. Estimation of the strength of a solution of KHO or NaHO by standard acid.

For these estimations $\frac{N}{1}$ or $\frac{N}{10}$ acid is employed in the laboratory, but in examinations an acid of any strength may be given; in any case the strength must be known.

10, 20, or 50 cc. of the solution is measured off in a pipette or measuring flask, and placed in a flask or beaker; some substance termed an "indicator" is then added, which indicates by its change of colour whether the solution is alkaline or acid; it is also advisable to dilute the solution with distilled water.

(The indicators employed are—

Litmus, blue with alkalies, red with acids,

Phenolphthalein, pink with alkalies, colourless with acids,

Turmeric, reddish brown with alkalies, pale yellow with acids,

Cochineal, reddish violet with alkalies, yellow with acids.

Methylorange, yellow with alkalies, red with acids. Litmus is not good when artificial light is used. Phenolphthalein should not be used with ammonia. Cochineal and Methylorange are not affected by carbonic acid.

The standard acid is added carefully till the "indicator" denotes that the solution is just acid. It saves time, if two quantities of the solution can be obtained, to run in the standard acid in quantities of 1cc. at a time, so as to get a rough idea of how much acid is required, and then to repeat the experiment, running in $\frac{1}{10}$ of a cc. towards the end of the experiment, thus—

Suppose 25cc. of the acid failed to turn the colour of the indicator, but 26cc. was obviously too much, the experiment is repeated with the second half of the solution, 24·5cc. of the acid is run in and then 2 drops (= $\frac{1}{10}$cc.) added, at a time, until the colour changes. In this way an accurate result can be obtained without unnecessary delay.

Suppose the problem was "To find the strength per litre of a solution of KHO, $\frac{N}{1}$ acid being given," as the acid is of "normal" strength the *nature* of the acid, whether HCl, H_2SO_4, etc., makes no difference. 25cc. of the KHO solution is taken, and one or two drops of an alcoholic solution of phenolphthalein added, the solution turning pink.

28cc. of acid failed to destroy the pink colour, but 29cc. rendered the fluid colourless.

The experiment is repeated with a second portion of 25cc. 28cc. of the acid is run in at once, and then two drops at a time, the colour goes at 28·3cc.

So 28·3cc. of the $\frac{N}{1}$ acid neutralise 25cc. of the solution; now 28·3cc. of $\frac{N}{1}$ acid neutralise 28·3 cc. of $\frac{N}{1}$KHO which contains 56 grams in the litre.

$\therefore$ 28·3cc. $\frac{N}{1}$KHO contains $\frac{56 \times 28{\cdot}3}{1000} = 1{\cdot}58$ grams of KHO.

And this is the quantity in 25cc. of the solution being analysed:

As 25cc. contain 1·58 grams
$\therefore$ 1000cc. contain 63·2 grams.

A similar procedure is adopted with the other acids and bases.

To take another example. "Find the strength of a solution of nitric acid, and calculate the amount of water to be added to it to bring it to $\frac{N}{1}$ strength, $\frac{N}{1}$ NaHO being provided."

25cc. of the nitric acid is taken, phenolphthalein added as before, and the $\frac{N}{1}$NaHO run in from the burette; when 30cc. has been added the solution is still colourless, but at 31cc. it is pink. Repeating the experiment with a second quantity of 25cc., the colour changes at 30·6cc.

Now 30·6cc. $\frac{N}{1}$NaHO neutralise 30·6cc. of $\frac{N}{1}HNO_3$, and $\frac{N}{1}HNO_3$ contains 63 grams in 1000cc.

$\therefore$ 30·6 contain $\frac{63 \times 30{\cdot}6}{1000} = 1{\cdot}9278$ grams HNO_3.

So 25cc. of the solution of HNO_3 contain 1·9278 grams HNO_3, and 1000cc. of the solution of HNO_3 contain 77·112 grams HNO_3.

Again, $\frac{N}{1}$ HNO_3 contains 63 grams in 1000cc. and 77·112 grams would be contained in $\frac{1000 \times 77{\cdot}112}{63} =$ 1224cc.

So 224cc. of water must be added to 1 litre of this HNO_3 to reduce it to normal strength.

OXIDATION BY $KMnO_4$.

The process of oxidation by a solution of potassium permanganate can be, at first, most profitably studied with the ferrous salts.

The reaction is represented by the equation—

$$10FeSO_4 + 9H_2SO_4 + 2KMnO_4 = 5Fe_2(SO_4)_3 + 2\,MnSO_4 + 2HKSO_4 + 8H_2O.$$

It will be seen that in the above equation 10 atoms of iron are oxidised to the ferric state by 2 molecules of potassium permanganate, or 1 molecule of $KMnO_4$ oxidises 5 atoms of Fe : now, two atoms of iron in the ferrous state require 1 atom of oxygen to convert them into the ferric condition, thus

$$2FeO + O = Fe_2O_3,$$

and 1 atom of Oxygen is equivalent, as regards valency, to 2 atoms of Hydrogen.

So that, as far as the above equation is concerned,

1 atom of O oxidises 2 atoms of Fe = 2 atoms of H.

$\therefore$ 1 molecule of $KMnO_4$ oxidises 5 atoms of H, and the weight of $KMnO_4$ (the hydrogen equivalent) required to form a $\frac{N}{1}$ solution of $KMnO_4$ is one-fifth of its molecular weight $= \frac{39 + 55 + 64}{5} = 31{\cdot}6$ grams.

So $\frac{N}{1}$ solution of $KMnO_4$ contains 31·6 grams in the litre.

Ordinary ferrous sulphate, $FeSO_4 + 7H_2O$, is apt to oxidise on keeping, so the ferrous ammonium sulphate $FeSO_4 + Am_2SO_4 + 6H_2O$, which keeps well, is preferable.

Suppose the strength of a $KMnO_4$ solution is to be determined—

0·7 gram of the above salt (after powdering and pressing between filter paper) is weighed out and dissolved in about 200cc. of distilled water which has been previously boiled, to free it from air, and acidulated with H_2SO_4.

The $KMnO_4$ is run in from a burette, as before, until the solution turns pink, *i.e.* until all the iron has been oxidised and the $KMnO_4$ is no longer decolorised.

Suppose 18cc. are required to produce a pink colour :

$FeSO_4 + (NH_4)_2SO_4 + 6H_2O = 56 + 32 + 64 + 36 + 32 + 64 + 108 = 392$; so 392 grams of the sulphate contain 56 grams of Fe,

and ·7 gram contains $\frac{\cdot 7 \times 56}{392} = 0{\cdot}1$ Fe.

$\therefore$ 18cc. oxidise 0·1 gram of Fe from the ferrous to the ferric state, and 1cc. oxidises $\frac{0{\cdot}1}{18} = {\cdot}00555$ gram of Fe; the solution is therefore slightly weaker than decinormal $\frac{N}{10}$, 1cc. of which would oxidise ·0056 grams of Fe.

If the strength of the $KMnO_4$ solution is known, it can be used to determine the amount of iron in any substance containing that metal, but the iron must be in the *ferrous* state ; if it is present as ferric iron it must be reduced by nascent hydrogen (Zinc and Sulphuric acid) or by passing SO_2 gas, etc , until the solution is colourless.

As an example 0·5 gram of an iron ore was dissolved, the solution reduced with zinc, the excess of zinc removed,

the solution required 42cc. of $\frac{N}{10}$ $KMnO_4$ to turn it pink.

1cc. of $\frac{N}{10}$ $KMnO_4$ oxidises ·0056 gram Fe.

$\therefore$ 42cc. of $\frac{N}{10}$ $KMnO_4$ oxidise ·2352 gram Fe.

So the ore contained in 100 parts $\frac{\cdot 2352 \times 100}{\cdot 5} = 47\cdot04$ % Fe.

$KMnO_4$ solution has the disadvantage that it cannot be used in the presence of HCl; it is also reduced by organic matter.

ACTION OF POTASSIUM PERMANGANATE ON OXALIC ACID.

The reaction between $KMnO_4$ and $H_2C_2O_4$ is represented by the equation

$$5(H_2C_2O_4 + 2H_2O) + 2KMnO_4 + 3H_2SO_4 = 10\,CO_2 + K_2SO_4 + 2\,MnSO_4 + 18\,H_2O.$$

Two molecules of $KMnO_4$ oxidise 5 molecules of Oxalic acid, which crystallises with 2 molecules of water.

Two molecules of $KMnO_4$ evolve 5 atoms of oxygen (see oxidation of Fe by $KMnO_4$, p. 524M). So one atom of oxygen oxidises one molecule of oxalic acid.

$$H_2C_2O_4 + 2H_2O + O = 2CO_2 + 3H_2O$$

and $\frac{N}{1}$ oxalic acid, *i.e.* $\frac{126}{2} = 63$ grams to the litre, will be exactly oxidised by an equal volume of $\frac{N}{1}$ permanganate, containing 31·6 grams in the litre, because 31·6 grams of $KMnO_4$ evolve 8 grams of Oxygen (see equation on p. 524M), which oxidise half a molecular weight or 63 grams of Oxalic acid, as seen in the equation above.

As an example, take the following problem :—"Find the strength of a solution of oxalic acid, $\frac{N}{1}$ $KMnO_4$ being given."

50cc. of the oxalic acid solution is taken, acidified with sulphuric acid, and heated to about 60°C. (as the reaction does not start at once in the cold) $\frac{N}{1}$ $KMnO_4$ is added till the fluid is just pink.

Suppose 45cc. of the $\frac{N}{1}$ $KMnO_4$ is required, 45cc. of

$\frac{N}{1}KMnO_4$ will just colour 45cc. of $\frac{N}{1}H_2C_2O_4$ which contains 45 × ·063 = 2·83 grams.

50cc. of the solution given therefore contain 2·83 grams, and 1000cc. of the solution given contain 56·6 grams of crystallised Oxalic acid, $H_2C_2O_4 + 2H_2O$.

For some purposes a solution of potassium bichromate is preferable to a solution of potassium permanganate, since it is not affected by the presence of hydrochloric acid or organic matter. The reaction is

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2KCl$$
$$+ Cr_2Cl_6 + 7H_2O$$

1 molecule of $K_2Cr_2O_7$ oxidises 6 atoms of Fe.

So $\frac{N}{1}K_2Cr_2O_7$ contains $\frac{78 + 104{\cdot}8 + 112}{6} = 49{\cdot}13$ grams in 1000cc.

There is no marked change of colour when the iron is completely oxidised with HCl and $K_2Cr_2O_7$, so that the solution is tested for the presence of a ferrous salt by withdrawing from time to time small drops of the liquid and mixing them on a white plate with drops of a weak, freshly-made solution of potassium ferricyanide ; as long as any ferrous salt remains, the mixture turns blue, but as soon as the oxidation is complete no colour is produced on mixing the drops. Hydrochloric acid is used to acidify the solution instead of sulphuric acid, in other respects the estimation of ferrous iron by bichromate can be carried out as described under potassium permanganate.

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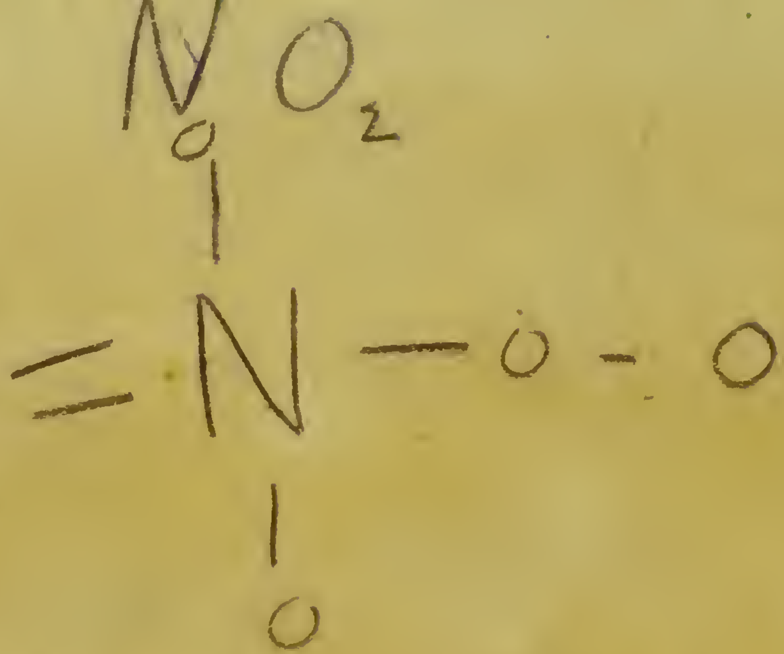
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